



IMPERIAL INSTITUTE
OF
AGRICULTURAL RESEARCH, PUSA.

CHEMICAL REVIEWS

GERALD WENDT, EDITOR

The Pennsylvania State College

VOLUME VI

BALTIMORE

1929

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THE SPECIFIC HEATS OF GASES AND VAPORS

A CRITICAL REVIEW OF METHODS AND RESULTS

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NOTATION

If we designate by c_p , c_v the heat capacity per gram at constant pressure and at constant volume, respectively, and by C_p and C_v the corresponding quantities per gram-mole, we have

$$C_p = Mc_p \text{ and } C_v = Mc_v$$

where M is the molecular weight of the gas. The normal calorie (15°) is assumed as the heat unit and temperatures are referred to the normal centigrade scale (hydrogen thermometer) but few authors take precautions in this connection on account of the moderate accuracy claimed for the result.

We can also write

$$\gamma = \frac{C_p}{C_v} = \frac{c_p}{c_v} \text{ and } \delta = c_p - c_v \quad (1)$$

It is obvious that it suffices to determine two of the four quantities c_p , c_v , γ and δ in order to find the others but knowledge of a third offers a valuable check.

FUNDAMENTAL QUANTITIES

The quantities γ and c_p are usually considered as the primary ones because c_v presents greater difficulties in experimental determination and the methods for calculating δ are unsatisfactory.

For example, to take the most favorable case, that of air, the values of c_p at one atmosphere obtained by different investigators

for the same temperature interval exhibit differences greater than one per cent and the values obtained over a temperature range can be fitted only by an undulating curve, as shown in Table 1. Furthermore while the values of γ for dry CO_2 -free air at atmospheric pressure in the neighborhood of 20° are sufficiently concordant to permit averaging (1.400 to 1.405), the values obtained at other temperatures and pressures exhibit discrepancies which can be characterized only as enormous. It is necessary, therefore, to consider the possibilities of calculating δ .

TABLE 1

t	-181	-75	+20	25	59	60	ca.230	ca.410
c_p	0 249	0 243	0 240	0 241 ₂	0 237	0 241 ₈	0 237	0 243

METHODS

1. Calculation of δ

In certain special cases precise values are available for the two coefficients of expansion

$$\alpha = \frac{1}{v_0} \frac{\partial V}{\partial T} \quad \text{and} \quad \beta = \frac{1}{p_0} \frac{\partial p}{\partial T}$$

and for such cases δ is readily obtained from the classical relation

$$\delta = \frac{T}{J} \frac{\partial p}{\partial T} \frac{\partial v}{\partial T}$$

in which all terms are known for 0° and 1 atm., and are comparatively easy to determine in general.

$\frac{\partial v}{\partial T}$ and $\frac{\partial p}{\partial T}$ may be computed in a general way from an appropriately selected equation of state; but it is first necessary to eliminate all equations, such as that of Van der Waals, which yield a value of β (and consequently of the internal pressure) which is independent of T .

A recent examination (1) of the behavior of the internal pres-

sure as a function of p and T has led to the expression¹ (CGS Units)

$$Mpv = RT \left[\left(\frac{v}{v + a} \right)^2 - 3.160 \frac{a v}{(v - a)^2} (4^x - 1) \right] \quad (2)$$

in which x is the reciprocal of the reduced temperature $\left(x = \frac{T_c}{T} \right)$;

$a = 0.0463 \frac{RT_c}{Mp_c}$; $R = 8.316 \times 10^7$ and $T_c = 273.1^\circ$.

For our present purposes this equation is somewhat inconvenient on account of the complexity of the calculations which it involves. Others have been suggested based more or less upon that of Van der Waals and upon the principle of corresponding states. One of these, proposed by D. Berthelot, yields results of sufficient accuracy, except close to the critical point, but cannot be used in the region of saturation. Another due to Callendar yields errors in the opposite direction. For example, for saturated steam at 100° and 1 atm.

$$M\delta = \begin{cases} 2.070 & \text{Equation of Berthelot} \\ 2.198 & \text{Equation of Callendar} \end{cases}$$

The mean 2.134 is not far from the true value 2.12.

A third relation proposed by Leduc may be expressed thus

$$Mpv = RT\varphi \quad (3)$$

which may be regarded as a definition of the relative molal volume φ , in terms of that of a perfect gas.

However, instead of taking for φ , the expression between brackets in equation 2, it may be treated as a function of T and p and the equation written in the form

$$C_p - C_v = M\delta = \frac{RT^2}{J} \alpha' \beta' \varphi = \frac{\left(\varphi + T \frac{\partial \varphi}{\partial T} \right)^2}{\varphi - p \frac{\partial \varphi}{\partial p}} \quad (4)$$

¹ A. Leduc, *Thermodynamique*, Doin, (1924), p. 192; and *Compt. rend.* 176, 1132 (1923). This equation reproduces very closely Amagat's data for CO₂ almost up to saturation and as high as 200 atm. and 100° , for example. It also faithfully reproduces the isotherms of O₂ up to 500 atm. but with significant departures at 1000 atm. doubtless because the variation of the co-volume is not properly taken care of by the equation.

with $\alpha' = \frac{1}{v} \frac{\partial v}{\partial T}$ and $\beta' = \frac{1}{p} \frac{\partial p}{\partial T}$. If p is of the order of 1 atmosphere (or if the reduced pressure $\pi \leq 0.1$), φ is given with sufficient accuracy by the expression

$$\varphi = 1 - mp - np^2 \quad (5)$$

in which m and n are functions of T and in most cases (normal gases) functions of the reduced temperature τ or better of its reciprocal x , $\left(= \frac{T_0}{T} \right)$

If we put $z = mp_0$ and $u = np_0^2$ equation 4 may be written

$$M \delta = \frac{R \left(\varphi - x \frac{\partial \varphi}{\partial x} \right)^2}{J \frac{\partial \varphi}{\partial \pi}} = \frac{R \left[1 + \pi \left(x \frac{\partial z}{\partial x} - z \right) + \pi^2 \left(x \frac{\partial u}{\partial x} - u \right) \right]^2}{J \frac{1 + \pi^2 u}{1 + \pi^2 u}} \quad (4a)$$

For the pressure range under consideration and for $\tau \leq 0.9$, $\pi^2 u$ is negligible.

For normal gases z is given by

$$z = 0.1 \sqrt{2x} [2x^3 + 1.45x(2-x) - 1]$$

and within the pressure limits under consideration we may assume² (2)

$$u = 2x^3 (x-1)$$

The values of δ employed in Table IV have been calculated by means of the above equations. The error in the values so calculated apparently should not exceed 0.2 per cent.

It should be noted that the partial derivatives, $\frac{\partial p}{\partial T}$ and $\frac{\partial v}{\partial T}$, apply to the same state of the gas, the calculation of δ in this way is not applicable to mean specific heats.

² A. Leduc, *Compt. rend.*, **148**, 548 (1909) and *Thermodynamique*, pp. 109 and 113, in which the case of the "abnormal" gas is also discussed.

2. Velocity of sound

The best method for determination of the specific heat ratio γ appears still to be that known as the "velocity of sound method" based upon the formula of Laplace

$$V = \sqrt{Ev} = v \sqrt{-\gamma \frac{\partial p}{\partial v}}$$

It is, however, not safe to assume the equation of state of a perfect gas in using the Laplace formula, a precaution not observed by many investigators, including some modern ones. In this manner for example (3) Wüllner (1878) found for CO_2 at 0° , $\gamma = 1.31131$ while the correct calculation gives 1.320.

TABLE 2

H_2	1.0006	CO_2	0.993	C_2H_6	0.988
N_2	0.9995	N_2O	0.9925	NH_3	0.9856
CO	0.9994	C_2H_4	0.992	Cl_2	0.983
O_2	0.9991	HCl	0.992	CN	0.978
NO	0.9990	PH_3	0.991	SO_2	0.9773
CH_4	0.998	H_2S	0.990		

The Van der Waals equation would obviously give a better result. It is, however, necessary to determine the constants of the equation from experimental data on the gas in the same region of pressures and temperatures.

Equation (2) is much more reliable; but the calculation is very laborious and for pressures of the order of one atmosphere it is more convenient to employ equations (3) and (5) which give

$$v \frac{\partial p}{\partial v} = \frac{p}{1 + np^2}$$

and since np^2 is negligible (4)

$$V = \sqrt{\frac{RT}{M} \gamma}$$

Having calculated γ with the aid of the perfect gas law, it is now corrected by multiplying it by the factor $\frac{1}{\phi}$, if the law of Avogadro has been assumed or by the factor $\frac{1}{\phi}$ if an experimental value for

the density has been utilized. Table 2 gives the values of φ_0 at 0° and 1 atm. (± 0.0002 where the fourth decimal is given).

The correction for departure from the perfect gas law amounts, therefore, to 5 per cent of γ for SO_2 , and to 4 per cent in the case of benzene at 100° and 1 atm.

The determination of V by the method of Kundt also requires certain precautions. The formula of Kirchhoff

$$V_{\text{obs.}} = V \left[1 - \frac{K}{d \sqrt{\pi N}} \right]$$

in which V is the velocity in free air, K is a constant and N is the frequency, is not valid according to some authorities (Lord Rayleigh, Helmholtz) unless the diameter, d , of the measuring tube ≥ 5 cm. K is usually taken as 0.65. Now most investigators have employed tubes of much smaller diameters and the various devices which have been used to eliminate K by using two or three different tubes are not valid since such an elimination itself assumes the validity of Kirchhoff's equation. Moreover K is a function of certain properties of the gas (e.g., the viscosity, which varies with T) and also of the nature of the tube, and it is probable that the proportionalities assumed are inexact. The correction is, therefore, unsatisfactory unless it is small; that is, unless the tube is wide and N is large.³

3. Method of Clement-Desormes

We shall pass over the grave difficulties created by the oscillations of Cazin which have not yet been satisfactorily resolved. The usual procedure is to produce a sudden expansion (< 5 cm. Hg) and it is necessary to calculate γ by the logarithmic formula (5).

³ If $d = 5$ cm. and $N = 435$ the correction amounts to 35×10^{-4} which is in the case of air 1.20 m/sec. This means that an error of 10 per cent in the correction is scarcely allowable since it is a systematic error.

Wüllner, with $d = 3$ cm. and $N = 2539$, failed to make any correction thus introducing an error of 0.5 per cent in γ for CO_2 . If the true value for N is 2535, Wüllner's CO_2 was not, as he supposed, free from air. Thus two errors were present, the first of which ≥ 0.3 per cent and the second possibly a little greater but impossible to evaluate. These two must have partially compensated the other one.

Even with an expansion equivalent to 10 cm. Hg for CO_2 at 0° , the error introduced by failure to correct for departure from the perfect gas law amounts to $\frac{\Delta\gamma}{\gamma} = -2.6 \times 10^{-4}$, which is negligible because a precision of 0.1 per cent is, at present, illusory. The correction is still small but necessary in the case of SO_2 at 0° , for example. It has been suggested that a series of expansions of decreasing magnitude be made and that the curve of values of γ thus obtained be extrapolated to zero expansion. This method, however, is of no value because of the increasing uncertainty in γ with decreasing expansion. This is the case, for example, in the experiments of Maneuvrier (formula of Reech).

4. Method of Lummer and Pringsheim

This method has been perfected by numerous investigators, and most recently by Partington. The correction for departure from the perfect gas law is especially large in this method: 0.5 per cent for CO_2 and 1.8 per cent for SO_2 at 15° . It is easily made with the aid of the relations discussed above. With the aid of an extra fine bolometric filament (Wollaston wire, $d \leq 2\mu$) and a rapid and sensitive galvanometer, Partington and Howe have sought to reproduce by means of the oscillations of the galvanometer mirror, those which occur within the gas.

The deflection was found to assume a constant value during a period of time varying with the nature of the gas, in some cases amounting to 10 seconds but not exceeding 2 seconds in the case of hydrogen.

It is difficult to follow the authors in their conclusion that this condition corresponds to a permanent equilibrium. It is rather an apparent or mobile equilibrium (Prevost) resulting from the fact that the heat supplied to the filament by radiation from its surroundings compensates for a short time, that which it loses to the gas cooled by the expansion. As a consequence the degree of cooling, and likewise the value of γ , is underestimated. This effect evidently increases with the diameter of the wire and it is on this account that Makower, using a wire of 30μ diameter found for saturated steam at $100^\circ\gamma = 1.303$, while the cyclic

method (Leduc *v. infra*) based upon the latent heat of vaporization and the vapor pressure gives $\gamma = 1.373$ and the experiments of Neyreneuf lead to the value 1.368 for the slightly superheated vapor. Aside from all other considerations, it is, therefore, necessary to increase slightly all values obtained by this method with very fine wires and to reject all those obtained with wires whose diameter attains 20 to 30 μ , for example. On the basis of these considerations it may be remarked that the great mobility of the hydrogen molecules favoring the exchange of heat between the wire and the gas would account for the decrease in the apparent equilibrium period.

One investigator has obtained a value for γ independent of the rate of the expansion employed. It is, however, difficult to see how a slow expansion could be adiabatic.

The substitution of a thermocouple for a bolometric wire (Moody) does not appear to offer any advantages.

5. Direct experimental determination of C_p

a. Method of mixtures (e.g., Regnault) and method of circulation (Delaroche and Bérard, E. Wiedemann, etc.). In this method the quantity of heat furnished to a calorimeter by a supposedly known mass of gas preheated to a known temperature is measured. The accurate determination of the mass of the gas is very difficult. The error in determining the fall in temperature of the gas is relatively unimportant, this fall being usually large.

The current of gas is necessarily rapid, which results in a significant pressure drop through the calorimeter even with the arrangement used by Regnault and especially with those employed in modern investigations (3). As a result an expansion takes place within the calorimeter resulting in an absorption of heat amounting in the case of air (according to two blank experiments by Regnault) to 1/160 of the heat carried by the gas when employing a preheat to 180° and a flow of 18 liters per minute. Since we are concerned here only with the order of magnitude of the heat effect due to the expansion of the gas it suffices to add a correction of 1/160 for experiments of this character. In this way we obtain for air, $c_p = 0.239$ and it is noteworthy that

this is precisely the value obtained by Wiedemann using a rate of flow of only 3 liters per minute but with a different type of apparatus.

It is obvious that this correction should increase with the velocity of flow. It should be very large, for example, in the experiments of Knoblauch and Jakob on the vapor of water in which a flow of 750 grams per minute was employed.

b. Constant flow. In the method of Callendar and Barnes on the other hand, the quantity measured is the heat which must be supplied to the gas by an electric current in order to heat it from t_1 to t_2 , while it is flowing at high velocity and consequently undergoing an expansion. The quantity of heat obtained is therefore too large. The values obtained by the method of constant flow are in fact larger than those obtained by the method of mixtures. The estimation of the exact magnitude of this error in either case is unfortunately difficult on account of the simultaneous presence of other errors. One is consequently reduced to averaging the results obtained by the two methods when similarly applied to the same gas.

6. Determination of C_v

a. Method of condensation of vapor. This method suggested by Bunsen has given in the hands of Joly a few very interesting results notably a variation of C_v with density which is confirmed by means of the equation of state. These results will be discussed below:

b. Velocity of sound. Dixon and his coworkers in their recent work do not claim to have bettered the precision of their predecessors at low or moderate temperatures, but they do claim to find the true value c , instead of the mean value c_h sought by previous investigators, usually with very discordant results. Dixon determines the time required for sound to travel the length of a long tube (straight or coiled) of lead, steel or silica according to the temperature. He found first that a tube 25-mm. diameter gave the same result when straight as when coiled. Using Kirchoff's correction, he found for air at 0° , $V = 331.8$ m/sec as compared with the accepted value 331.5. This con-

cordance is reassuring. γ was computed and then C_p and C_v with the aid of Berthelot's equation.⁴

In spite of the great difficulties connected with such experiments at very high temperatures, the results appear to be more reliable than those obtained by the following method.

7. *The explosion method*

In this method the explosive mixture receives a supposedly known amount of heat which suffices to raise the final system to a certain pressure which can be assumed to be a simple function of T if the composition of the final mixture is known at the moment of attaining the maximum temperature.

In reality this composition varies in an unknown manner with time, and though the mean heat capacity of the mixture is approximately known, it is not possible to calculate with any feeling of security the heat capacity of each gas in the mixture. This state of affairs justifies the attempts of Pier to *measure* the actual maximum temperature with the aid of a bolometer instead of attempting to calculate it from the measured pressure. Ingenious instruments were devised for correcting for the loss of heat (e.g., by an automatic pressure recorder) so that even though the values found for the specific heats of the gases are not satisfactory for the purposes of the scientist, they do make it possible to calculate the temperature and pressure developed in an analogous explosive mixture of the same gases in different proportions which has certain useful applications in ballistics.

8. *Examination of the specific heat data*

Atmospheric air under ordinary conditions and dry air at 0°.
It is not possible to determine accurately the so-called normal

⁴ The question has been asked as to whether the perfect gas law may be safely employed under conditions of high pressure if the temperature is also high. Application of equation (4a) gives for CO_2 at 1000° ($x = 0.24$) and 1 atm., $C_p - C_v = \frac{R}{J} \times 1.0003$ that is practically $= \frac{R}{J}$. At 100 atm., however, we would have approximately $C_p - C_v = 2.05$ the same as for CO_2 at 0° and 1 atm. The error would be still greater at 2000° under 2000 atm.

velocity of sound; that is, the velocity in open air. Measurements in large tubes are much more accurate. The Violle correction for the tube diameter may be regarded as reliable but the humidity correction according to the formula of Regnault

$$V_{Dry} \left(1 + A \frac{f}{H} \right)$$

with $A = 0.1875$ is very inaccurate.

In 1913, Violle accepted $A = 0.16$ and obtained $V_0 = 331.36$ m/sec.

In practice it is convenient to employ Leduc's equation for gas mixtures (6).

$$K_{\text{Mix}} = \frac{\sum k_{\alpha} r_{\alpha}}{\gamma - 1}$$

in which r_{α} is the richness of the mixture in the gas α and k_{α} the value (for this gas) of the expression

$$K = \frac{(\beta T)^2 (1 + n p^2)}{\varphi}$$

This is equivalent to the use of Regnault's equation with $A = 0.15$. It is necessary in addition to make two smaller corrections for CO_2 and for the mercury-in-glass temperature scale, which gives finally

$$V_0 = 331.5 \pm 0.1 \text{ m/sec.}$$

Equation (5) then gives $\gamma_0 = 1.402$, which may be compared with

1.403	Guéritot 1912
1.403 ₄	(17°) Partington 1913
1.402 ₆	(20°) Miss Schields 1917
1.403 ₁	(0°) Hebb 1919

On the basis of the best values we may take $\gamma_0 = 1.403$ and $\gamma_{100} = 1.401$, the latter being based upon an assumed linear variation with t and being therefore less certain. The coefficients of expansion α and β are accurately known and lead to

$$(c_p - c_v)_0 = 0.0689,$$

whence $(c_p)_0 = 0.240_0$ and $(c_v)_0 = 0.171_1$. For a molecular weight of 28.98 these correspond to $(C_p)_0 = 6.95_8$ and $(C_v)_0 = 4.95_8$. It is to be noted that the method of mixtures gives at $25^\circ c_p = 0.237$ (e.g., Scheel and Heuse, Eggert) instead of 0.241 by the constant flow method (Swann, Scheel and Heuse). This confirms previous observations. We must conclude, therefore, that the value of Swann $(c_p)_{100} = 0.243$ and that of Thibaut, $(c_p)_{350} = 0.245$, are too large. Volume V of International Critical Tables gives a tabulation of the results of various investigators between -185° and $+280^\circ$, and for pressures up to 220 atm. Within this region the data show that

$$\frac{\partial c_p}{\partial p} > 0 \text{ and } \frac{\partial c_p}{\partial T} > 0$$

We may note further that c_p (Witkowsky) and c_v (Bennewitz and Splitberger) (7) each becomes infinity at the critical point.

It may be noted further that the values calculated by Lussana are in general much larger than the experimental values of other investigators. Thus for 100° and 100 atm. Lussana gives $c_p = 0.395$ instead of 0.265.

As regards γ , while at 0° Witkowsky and Koch find that it varies almost linearly with the pressure between 25 and 200 atm. ($\gamma = 1.83$), Koch finds that at -79.4° it passes through a maximum at 150 atm. ($\gamma = 2.47$) and falls again to 2.33 at 200 atm.

Various gases at 15° and 1 atm. The value of γ is rarely known to 0.001 and in some cases the value is not known beyond the second decimal. Even in such cases, however, calculation through γ and δ is to be recommended. One obtains in this way table 3.

Molal heat capacity at 15° and 1 atm. Calculated from γ and δ . At very low temperatures it is best to utilize the experimental C_p values at atmospheric pressure as determined by Scheel and Heuse and others, and to calculate δ from equation (4). The second decimal is here uncertain on account of experimental difficulties.

According to the data of those authors the specific heats for certain gases decrease with increase in temperature in the region

-180° to -50° , while above 0° we have in nearly all cases $\frac{\partial c_p}{\partial T} = 0$ and $\frac{\partial c_v}{\partial T} > 0$ at atmospheric pressure. Such a result would ordinarily be attributed to important experimental errors; but the phenomenon appears also in the case of CO_2 at ordinary temperatures and high pressures, according to Lussana (e.g., $c_p = 1.47$ at 13.2° and 0.386 at 114.9° under a pressure of 20.5 atm.). According to Knoblauch and Mollier the same is true for water vapor.

TABLE 3

GAS	$M\delta = c_p - c_v$	γ	c_p	c_v
A	1 994	1 66 ₈	5 00	3 00
H ₂	1 987	1 410	6 83	4.84
N ₂	1 995	1.404	6 94	4 94
O ₂	1 995	1 401	6 97	4.97
NO	1 996	1.400	6 99	4 99
CO	1 995	1.404	6 94	4.94
CH ₄	2 004	1 31	8 47	6 47
CO ₂	2 041	1.304	8 75	6.71
N ₂ O ₂	2 050	1 303	8.82	6.77
C ₂ H ₄	2.057	1 255	10.07	8 03
HCl	2 057	1 41	7.07	5 02
C ₂ H ₂	2.057	1 26	9 97	7 91
C ₂ H ₆	2 086	1 22	11.6	9 5
H ₂ S	2 092	1 32	8 63	6 54
NH ₃	2.108	1 31	8.91	6 80
Cl ₂	2 135	1 35 ₈	8 15	6.0 ₁
CN	2.170	1 25 ₆	10.6 ₈	8.4 ₈
SO ₂	2 18 ₈	1 29	9.7 ₁	7 5 ₈

In spite of the satisfactory nature of the curves obtained, it seems justifiable to question these results on account of the enormous gas velocities employed, the flow amounting to more than 750 g./min. This appears to be the more justifiable in the light of Holborn and Henning's values at atmospheric pressure which fail to exhibit any minimum. It might be objected that these latter experiments do not extend below 250° while the minimum to be expected is not very pronounced and should lie at about 190° . But it should be noted that at a given temperature the experimental values are uncertain to 2 per cent which is the difference found between 100° and 190° .

In this connection, it is interesting to compare (table 4) some values by Knoblauch and Mollier with those of Holborn and Henning. The existence of such a minimum is furthermore inconsistent with the calculations of Leduc (8) for saturated and superheated vapor between 100° and 160° and for pressures up to 4 atm. based upon the vapor pressure data of Holborn and Henning up on the latent heat values of Henning, and upon the curves of compressibility (in reduced coördinates) of the vapor up to the saturation point (see equations 3, 5, etc.). It should be noted that the values of γ calculated by the same method (the cycle method) are materially greater than those ordinarily accepted. Thus at 100° $\gamma_s = 1.373$ in good agreement with the value deduced from the velocity of sound according to Neyreneuf

TABLE 4

	KNOBLAUCH AND MOLLIER	HOLBORN AND HENNING
100°	0 48 ₂	
200°	0 47 ₁	0 46 ₅ (extrapolated)
400°	0 49 ₀	0 47 ₃

(9) by means of equation (5), namely, $\gamma = 1.368$ for the slightly superheated vapor.

In conclusion, even if we reject the more doubtful series of measurements as well as those involving the most serious experimental difficulties, it is scarcely possible to be certain of a precision better than 1 part in 200 for pressures other than atmospheric at very high or very low temperatures.

For c_v the uncertainty is even greater whether the values are obtained by the explosion method or deduced from γ or c_p by combination with δ .

Partington and Shilling (10) have constructed specific heat-temperature curves from the best available data in particular the c_p data of Knoblauch and Mollier and the c_v data of Pier between 2000° and 2500° as recalculated and materially modified by Siegel.

It should be pointed out that the values of c_p being for 1 atm. this will also be the case for the values of c_v calculated by equation

(1), while the c_v values obtained by the explosion method correspond to a wide variation in pressure.

It is, therefore, not justifiable to deduce c_p values from these c_v values unless they are expressed as a function of T and p . It is possibly for this reason that the curves obtained for water vapor have such a peculiar form, since the high temperature values are deduced from the explosion data. Dissociation is, however, also doubtless a factor, since the curves for CO_2 computed from similar data do not exhibit the same character.

9. Variation of c_v with density

The experiments of Joly (11) using with a high degree of perfection the method of vapor condensation suggested by Bunsen deserve special mention. The values shown in table 5 were obtained for the mean specific heat (at substantially constant

TABLE 5

d , g/cm ³	0 0387	0 077	0 118	0 144
c_v	0 171 ₄	0 184	0 194	0 202

volume) of CO_2 between 12° and 100° . Joly represents his data by the following formula:

$$(c_v)_{12}^{100} \pm 1\% = 0.165 + 0.2125 d + 0.340 d^2$$

Now, if we use the classical equation

$$\frac{\partial c_v}{\partial v} = \frac{T}{J} \frac{\partial^2 p}{T^2}$$

together with equation (2), we obtain

$$\frac{\partial c}{\partial d} = \frac{12.07}{M} x^2 \times 4^x \frac{a}{1 + a d}$$

whence on integrating

$$c = c_0 + 0.274 x^2 4^x \frac{a d}{1 + a d}$$

where c_0 corresponds to $d = 0$.

The calculation gives for $d_1 = 0.05$ and $d_2 = 0.15$, $c_2 - c_1 = 0.030$.

Now experiment gives $c_1 = 0.176$ and $c_2 = 0.204$. The difference, 0.028, shows satisfactory agreement with the calculated value and it is safe to assume that the function $c = F(d)$ is a hyperbola at least up to $d = 0.15$ and probably further.

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REACTION LIMITS, REACTION REGIONS AND REACTION SPACES

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INTRODUCTION

Since Humphry Davy in 1815 determined the range of explosibility of mixtures of "firedamp" with air (1), many researches have been made on the *limits of inflammability* of mixtures of a combustible gas or vapor and air or oxygen. The extensive literature relating to this subject has been collected in several publications (2). For a survey of the principal experimental results and the theoretical views which bear upon the subject, we can, therefore, refer to those reviews.

Next to these investigations, which are also of great practical value, the *dust explosions* have given rise to much research work, also on account of their disastrous results (3). Only a few limits have been determined.

It is also well known that a reaction, started locally in a mixture of *solid substances*, may propagate itself through the whole mass, if the composition of the mixture is suitable. We have only to call to mind the old gun powder, made from charcoal, sulfur and saltpeter, and the different mixtures in fireworks, etc. As lecture experiments there may be cited the propagation of the reaction in mixtures of iron and sulfur, of magnesium and silica and the like. The importance of the study of such reactions has become obvious since Hans Goldschmidt (4) applied the aluminothermic reduction to his "thermites." When reading W. Prandtl's "Thermitreaktionen" (5) we get an impression of the great variety of reactions taking place in a similar way.

If we restrict ourselves in the first place to mixtures of two substances, we observe—just as with mixtures of a combustible

gas or vapor and air or oxygen—that the reaction takes place only between two *limits*, which we have called *reaction limits*. Such limits were determined by us for instance in the case of iron, magnesium or aluminium and sulfur (6) (7), and potassium dichromate and sulfur or aluminium (8). In the case of ammonium dichromate and iron or sulfur (9) only one limit is observed, as the reaction started in pure ammonium dichromate will also propagate itself.

Although the study of the reactions between binary mixtures of solid substances presents many interesting points of view, such as the determination of velocities (43), we shall confine ourselves here chiefly to ternary and quaternary mixtures. From these we choose those containing only gases or vapors and those containing only solid substances.

I. TERNARY MIXTURES

A. First of all we shall consider reacting mixtures of three gases. If we regard air as one substance (viz. less reactive oxygen) our attention is drawn first to explosions of mixtures of *two combustible gases or vapors and air*. Such mixtures have been studied exhaustively since H. Le Chatelier published (10) his well known formula $\frac{n'}{N'} + \frac{n''}{N''} = 1$. In this formula n' and n'' are the volumes of the two combustible gases which, mixed together with the quantity of air needed to make the total volume 100, just produce an inflammable mixture. N' and N'' are the limits of inflammability of the two gases taken separately. Le Chatelier considered this relation almost as a matter of course. He applied it in the first place to determine the percentage of methane present in mine air. He added so much of a combustible gas, of which the lower limit of inflammability is known, that the lower limit of inflammability of the mixture was reached. As N' , n'' and N'' were known, he could calculate n' .

P. Eitner (11) remarked that Le Chatelier's formula indicates that a combustible gas, mixed with other gases, produces the same volume of inflammable mixtures gas-air, as when alone. But, he adds, then the formula must also hold good for mixtures

of more than two combustible gases. Thus the general form will be (12):

$$\frac{n'}{N'} + \frac{n''}{N''} + \frac{n'''}{N'''} + \dots = 1$$

Le Chatelier and O. Boudouard (13) found the formula to apply to mixtures of CO and C_2H_2 . Slight deviations were observed with mixtures of CO and H_2 .

Inflammable mixtures were found to be:

CO	15.9	12 0	7 75	4.3	0
H_2	0	2.7	5.50	7.6	10.0
Thus $\frac{n'}{N'} + \frac{n''}{N''} =$	1	1.025	1.04	1 02	1

Eitner remarks that the relation will only hold if the gases do not hinder each other's inflammability. Therefore he does not expect that it will prove exact for the upper limit of inflammability, as in that case there is not a sufficient quantity of oxygen to burn both gases completely. In fact he calculates for the upper limit of inflammability of water gas (49.15 per cent CO, 49.85 per cent H_2 , 1 per cent air): $\frac{n'}{N'} + \frac{n''}{N''} = 0.949$.

Among those who have tested Le Chatelier's formula should be mentioned especially H. F. Coward, Ch. W. Carpenter and W. Payman (14) and A. G. White (partly with T. W. Price) (15).

It was especially White who, in the course of his extensive researches, has found many deviations from this formula.

Graphical representation

If we consider the quantities of the two combustible gases as coördinates (16) we are able to represent the limiting mixtures by points in a plane. If the mixtures obey the formula of Le Chatelier we get a straight line. For if we consider n' and n'' as variables, *the formula is the equation of a straight line*, N' and N'' , the lower or upper limits of inflammability, being the intercepts on the axes. An example of nearly straight lines for the lower and upper limits is afforded by the experiments of Coward,

Carpenter and Payman (14) with mixtures of CO and H_2 (fig. 1). The region between those lines and the two axes we have called

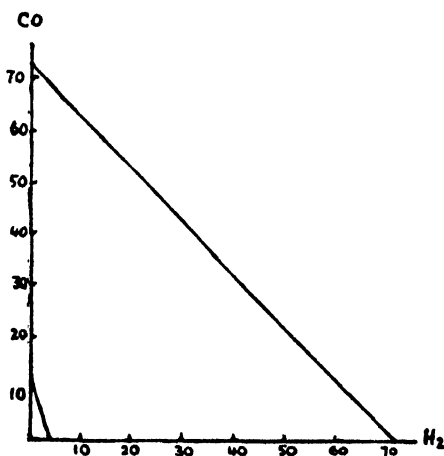


FIG. 1. EXPLOSION REGION $CO-H_2-AIR$

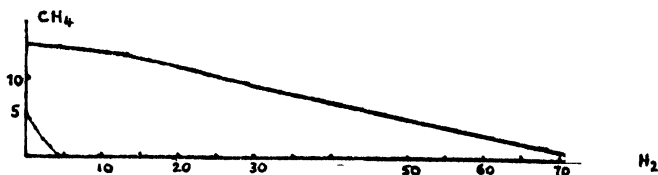


FIG. 2. EXPLOSION REGION CH_4-H_2-AIR

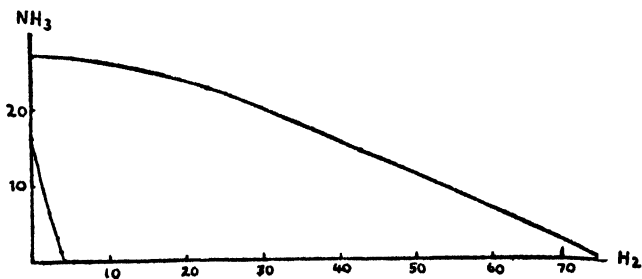


FIG. 3. EXPLOSION REGION NH_3-H_2-AIR UPWARD PROPAGATION

explosion region. All the mixtures represented by points outside this region are non-inflammable.

More perceptible deviations from straight lines are found if we represent graphically White's results (17) with mixtures of CH_4 and H_2 (fig. 2) or with mixtures of NH_3 and H_2 (fig. 3). But in the latter case ammonia shows limits of inflammability only with upward propagation. For if we represent graphically his results

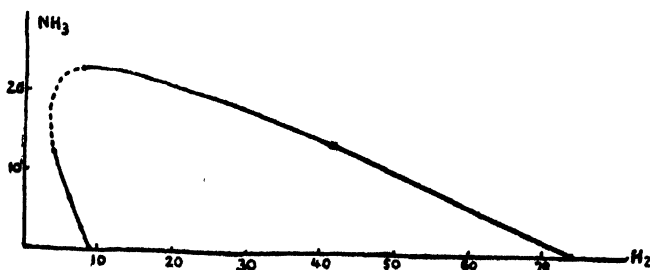


FIG. 4. EXPLOSION REGION NH_3 - H_2 -AIR DOWNWARD PROPAGATION

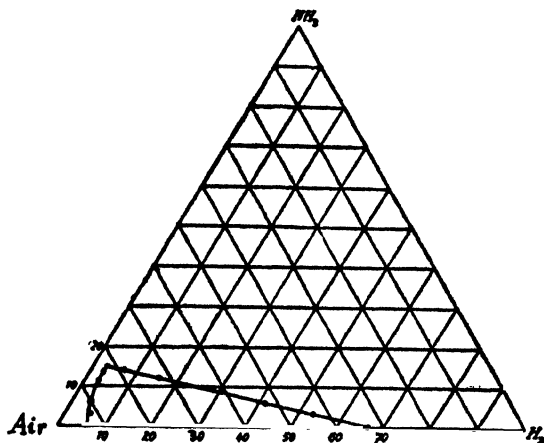


FIG. 5. EXPLOSION REGION NH_3 - H_2 -AIR

with downward propagation we get the curve shown in figure 4. As we see, the explosion region does not reach the vertical axis, which means that in the case of downward propagation (under the circumstances of White's experiments), no mixture of NH_3 and air alone will explode.

These graphical representations show the deviations from Le

Chatelier's formula much better than tables of figures; even when these tables give the deviations in per cents.

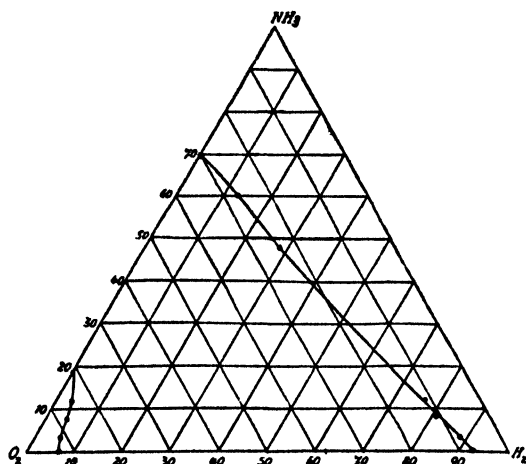


FIG. 6. EXPLOSION REGION $\text{NH}_3\text{--H}_2\text{--O}_2$

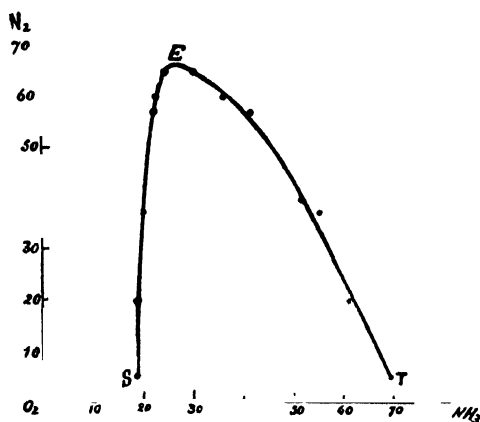


FIG. 7. EXPLOSION REGION $\text{NH}_3\text{--N}_2\text{--O}_2$

But they also show clearly the influence of different circumstances, such as: downward propagation and upward propagation.

How much the extent of an explosion region may be changed

when replacing air by oxygen is shown by the following diagrams figure 5 and figure 6 (18). Here we have represented the results in equilateral triangles.

We shall now consider mixtures of *one combustible gas (or vapor), one non combustible gas (or vapor) and air (or oxygen)*.

Let the non combustible substance be nitrogen and the combustible one ammonia. How the limits of inflammability of

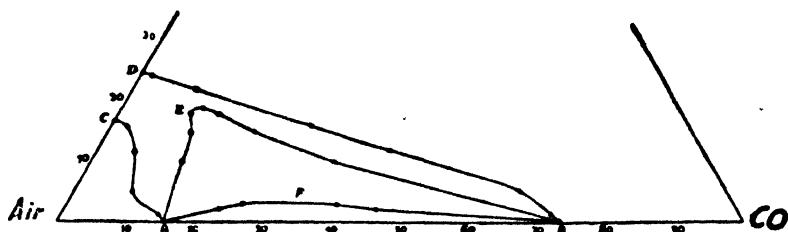


FIG. 8. THE EXPLOSION REGIONS $\text{CO}-\text{CHCl}_3-\text{AIR}$, $\text{CO}-\text{CH}_2\text{Cl}_2-\text{AIR}$ AND $\text{CO}-\text{CH}_3\text{Cl}-\text{AIR}$

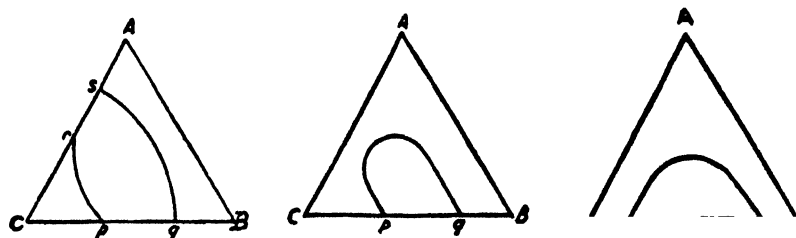


FIG. 9. THREE TYPES OF EXPLOSION REGIONS OF FREQUENT OCCURRENCE IN PRACTICE

ammonia-oxygen-mixtures change when gradually replacing the oxygen by nitrogen is shown in figure 7. The limits approach each other and coincide at about 32 per cent of oxygen (19).

In the same way the vapor of carbon tetrachloride makes the limits of inflammability of methane in air coincide when the vapor content reaches a certain figure.

In our experiments (20), with a tube of about 1.5 cm. internal diameter, a small spark and downward propagation, a vapor content of 7.8 per cent was sufficient to make the mixture of

methane and air non inflammable; in those of H. F. Coward and G. W. Jones (21) with a tube of about 5 cm. internal diameter, a flame of a spirit lamp as igniter and upward propagation a vapor content of about 12 per cent CCl_4 was necessary. The difference between these figures illustrates the influence of different experimental conditions on the extent of the explosion region (22). Carbon tetrachloride also narrows the limits of inflammability of hydrogen-air-mixtures (23) and acetylene-air-mixtures (23) and

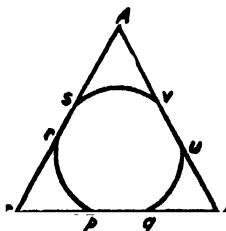
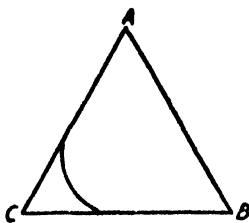


FIG 10

FIG. 11. TWO OF THE THREE CASES
ARE ENDOTHERMICFIG. 12. ONE OF THE THREE CASES
IS ENDOTHERMIC

has a strong extinguishing influence on the inflammability of carbon monoxide-air-mixtures (24). The explosion region CO-air- CCl_4 is therefore very small.

That of carbon monoxide, air and chloroform vapor (24) is also a small one (fig. 8). That of carbon monoxide-air-methylene chloride is larger and already approaches somewhat the left side of the triangle. The explosion region carbon monoxide-air-methyl chloride reaches the left side of the triangle; the lower limit of inflammability of CH_3Cl -air mixtures is indicated in

figure 8 by C, the upper limit by D. Figure 8 thus shows clearly that the incombustibility of CCl_4 decreases when chlorine is replaced by hydrogen.

The explosion region $\text{CO-air-CH}_2\text{Cl}_2$ appears to be intermediate between that of CO-air-CHCl_3 and that of $\text{CO-air-CH}_3\text{Cl}$. When a vapor shows an explosion region with CO or another combustible gas resembling that of $\text{CO-air-CH}_2\text{Cl}_2$, we have to do with a substance which, although not combustible, tends to become so. It may become combustible at a somewhat higher temperature.

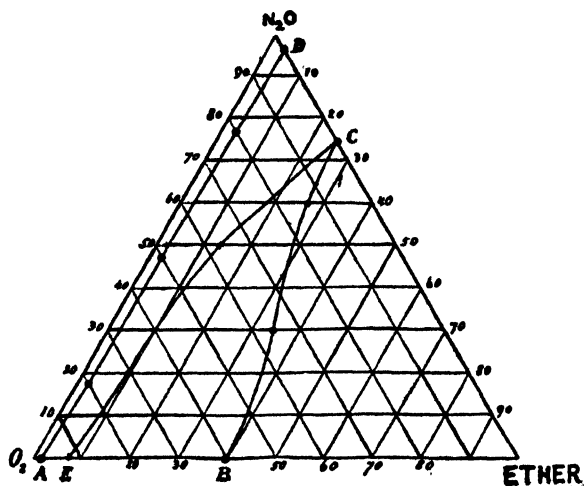


FIG. 13. EXPLOSION REGION $\text{N}_2\text{O-ETHER-O}_2$ (AIR)

In what measure the region approaches the left side of the triangle will depend on the combustibility of the gas with which we mix the methylene chloride vapor (25).

The three types of explosion regions drawn in figure 8 and also, in outline, in figure 9 are to be found in the case where the three gases A, B and C can react with each other and also C with A and C with B, but not A with B. This case, therefore, is not the simplest one. But it has been treated here in the first place, because in practice it occurs frequently.

From a systematic point of view it would have been better to begin with mixtures of *three gases which can react upon each other*

and also two by two. Such a case is represented in outline by figure 10; it has not been investigated experimentally.

As an example may be cited the system hydrogen-oxygen-sulfur vapor (26).

If the *three gases* are *endothermic* and the impulse (for instance a spark) is strong enough to start in each of them a reaction which propagates itself (without one or two of the others being present), then the explosion region will fill the whole triangle; if two of the

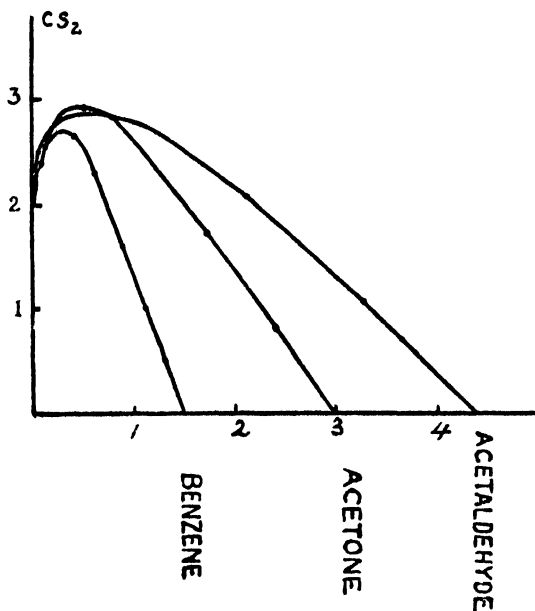


FIG. 14

three *gases* are *endothermic* or only *one* of them, we can expect explosion regions represented in outline in figures 11 and 12 (26).

Interesting explosion regions will be found, using, for instance, mixtures of acetylene, carbon disulfide vapor, nitrogen oxide or nitrous oxide with other gases.

A few cases have been studied already. We mention in the first place the systems: ether vapor-oxygen (or air)-nitrous oxide and chloroform vapor-oxygen-nitrous oxide (27). But

in these cases only a small spark was used, which did not start a reaction in nitrous oxide alone.

The explosion regions $(C_2H_5)_2O-O_2-N_2O$ and $(C_2H_5)_2O$ -air- N_2O are represented in figure 13, viz., ADCB and ADCE. When the spark is strong enough to start in nitrous oxide (without ether vapor) a reaction which propagates itself, the line AD will revolve round A, and cut the left side of the triangle.

The system chloroform-oxygen-nitrous oxide investigated in the same way (as the other two mentioned above) appeared to have no explosion region.

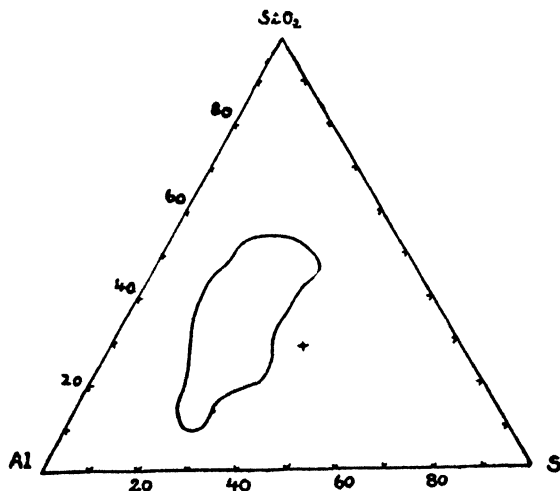


FIG. 15. REACTION REGION Al-SiO₂-S

Some experiments with carbon disulfide have been made by A. G. White (28) who determined the lower limits for the propagation of flame downward in mixtures of acetone, benzene and acetaldehyde with carbon disulfide and air. These limits are represented by me (29) in figure 14. The curves show an interesting flexion.

Of practical value will be, for instance, investigations of the systems: acetylene-acetone vapor-air and such like, with a view to the question of not dangerous, dissolved acetylene; acetylene-saturated hydrocarbons (for the manufacture of carbon₄black);

nitrogen oxide-carbon disulfide-nitrogen (or carbon dioxide) to supply a source of a constant actinic light, etc. The determination of the velocity of reaction in different parts of the reaction region will in several cases give an indication as to the mixtures to be used for special purposes.

B. We will now turn our attention to *mixtures of three solid substances*. Here we have been able to realize (30) the reaction region in its simplest form (a closed reaction region), using

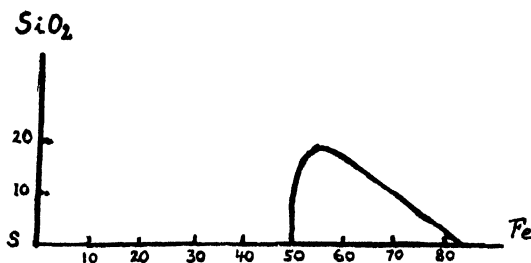


FIG. 16 REACTION REGION Fe-S-SiO₂

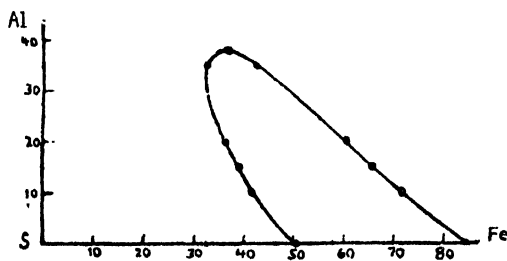


FIG. 17. REACTION REGION Fe-S-Al

mixtures of dried silica powder, flowers of sulfur and fine aluminum powder. A mixture of iron and sulfur (1 Fe:1 S) served as a fuse, which was, in its turn, ignited by means of a small gas flame. The reaction region is depicted in figure 15. Its extent depends on the conditions of the experiment. So an extension towards the Al-S axis is therefore to be expected with the use of a more powerful igniter.

That the region is of a greater extent under the conditions given

by Kühne (31) and Holleman (32) follows from the fact that the mixture 200 g. Al, 250 g. S and 180 g. SiO_2 falls outside the region determined above.

It is our intention to measure the reaction velocity in different parts of the region.

The region $\text{B}_2\text{O}_3\text{-Al-S}$ and similar ones will also be investigated. The three types of reaction regions, which we have observed, using mixtures of carbon monoxide and air with the vapor of

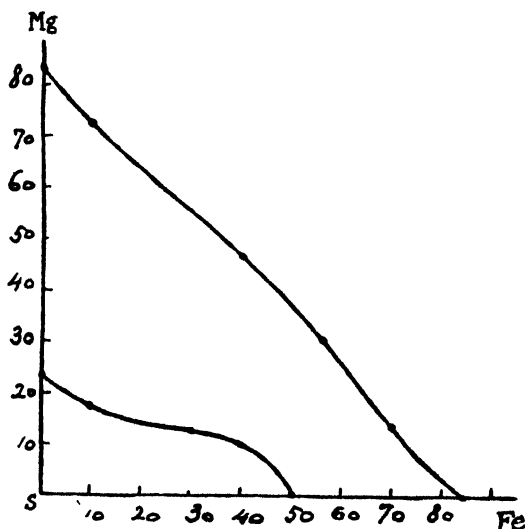


FIG. 18. REACTION REGION Fe-S-Mg

chloroform, methylene chloride or methylchloride (figs. 9 and 10), have been realized also with the following systems (33): Fe-S- SiO_2 (figure 16), Fe-S-Al (figure 17) and Fe-S-Mg (fig. 18). The substances were used in the form of powders; the mixtures were fired by means of a mixture of iron and sulfur (1Fe:1S) to which a small flame was applied.

The influence of the size of the particles of the reacting substances and of the nature of the igniter has been studied with the system Fe-S-Al (34). Thus we see the possibility of a closed reaction region extending itself to one or more of the sides of the

triangle. Extension to one side may give as results figures 16 and 17. Cases of extension to two sides of the triangle are drawn in figure 18 and figure 19 (8). Extension to all three sides (fig. 20) has been observed with potassium dichromate, sulfur and aluminium which react upon each other and also two by two (8).

Interesting reaction regions will be found, when using *endothermic* solid substances (compare p. 26). If one of the substances is endothermic and the impulse is strong enough to start a reaction which propagates itself also in the pure endothermic

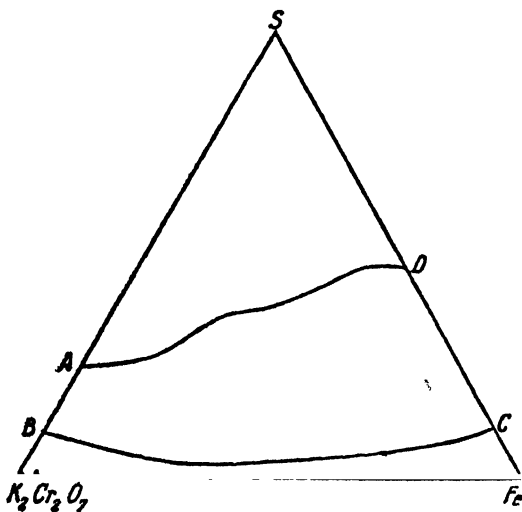


FIG. 19. REACTION REGION $K_2Cr_2O_7$ -Fe-S

substance, then the reaction region will extend to the corner of the triangle representing that substance.

This may also be observed when an exothermic substance decomposes (but not into the elements) with evolution of so much heat that the reaction, started in one part of the substance, propagates itself through the whole mass. A well-known example is ammonium dichromate. Mixtures of this substance with potassium chloride and potassium sulfate produce a reaction region drawn in figure 21 (9). If we make mixtures of ammonium dichromate with two substances which react upon each other, for instance iron and sulfur, the reaction region must become much

larger. For it must then reach the opposite side of the triangle. The reaction region is depicted in figure 22 (9). A narrowing occurs at HK. This narrowing gave rise to an investigation communicated on page 41.

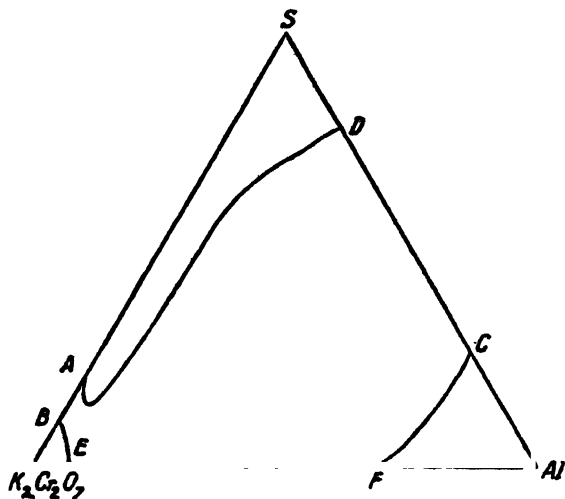


FIG. 20. REACTION REGION $K_2Cr_2O_7$ -Al-S

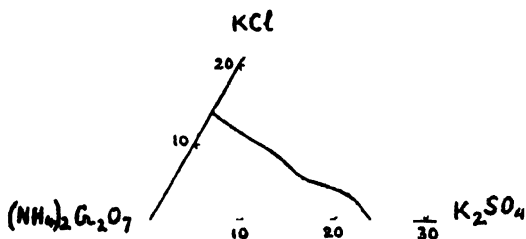


FIG. 21. REACTION REGION $(NH_4)_2Cr_2O_7$ -KCl- K_2SO_4

The limiting curve DEKC also shows a bulge at E. Now bulges had already been observed with reacting gas mixtures (see for instance figure 14). We hope to be able to account for the bulge at E by a quantitative investigation of the reactions taking

axes. If the formula holds good not only for the lower but also for the upper limits, we shall get an explosion space enclosed by five planes, *viz.*: the three coördinate planes and the two planes

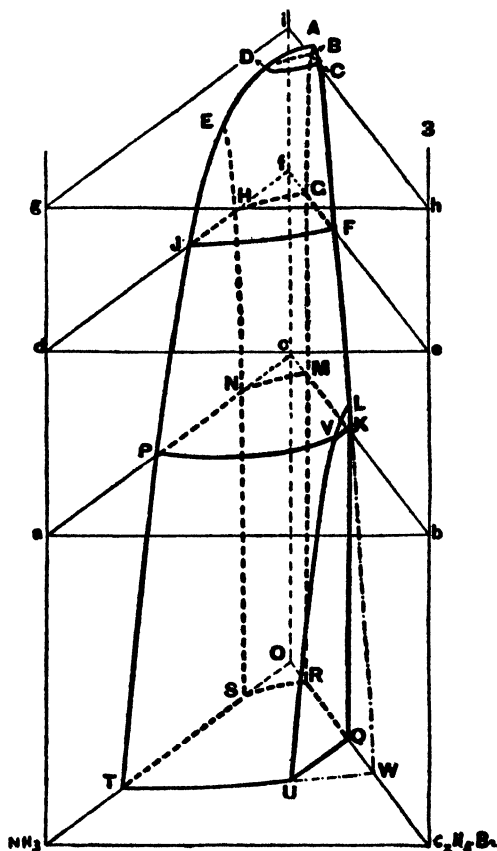


FIG. 23. EXPLOSION SPACE $\text{NH}_3\text{--C}_2\text{H}_5\text{Br--O}_2\text{--N}_2$

represented by Le Chatelier's formula (35). In general, however, we may expect an explosion space enclosed by a partly curved surface.

The case of two combustible gases or vapors, one noncombustible gas and oxygen has been studied by taking ethyl bromide vapor, ammonia, nitrogen and oxygen (19).

The explosion space is represented by figure 23. Its base is formed by a triangle of which the corners represent NH_3 , $\text{C}_2\text{H}_5\text{Br}$ and O_2 . S and T represent the limits of inflammability of NH_3 with oxygen, R indicates the lower limit of inflammability of $\text{C}_2\text{H}_5\text{Br}$, the upper limit W cannot be determined, as the oxygen is saturated with ethyl bromide vapor at Q.

If we now draw a triangular prism, the base of which is formed

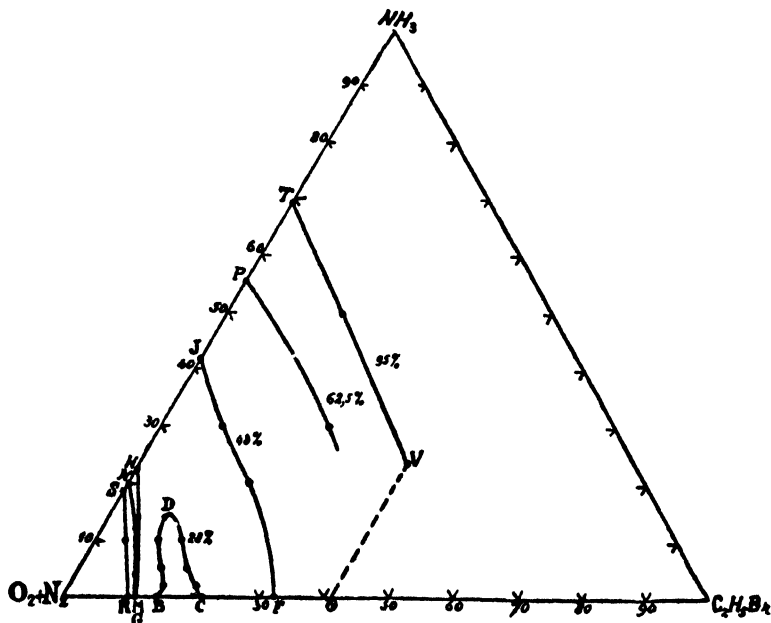


FIG. 24. EXPLOSION SPACE $\text{C}_2\text{H}_5\text{Br}-\text{NH}_3-\text{O}_2-\text{N}_2$: HORIZONTAL SECTIONS AT DIFFERENT PERCENTAGES OF OXYGEN

by the triangle, we can measure the nitrogen upwards along the parallel edges of the prism, which are at right angles to the plane of the base.

Making horizontal sections at different percentages of oxygen, we get different explosion regions of which four have been drawn in figure 24.

If the O_2-N_2 -mixture contains 95 per cent of oxygen the explosion region is RSTVQ. The line of the upper explosion limits TV ends in V, because the gas mixture is then saturated with

ethyl bromide vapor. Also when the O_2 - N_2 -mixture contains 62.5 per cent of oxygen the line of the upper limits (beginning in P) does not reach the horizontal side of the triangle. If 43 per cent of oxygen is present in the O_2 - N_2 -mixture the explosion region is limited by the curves HG and JF and two sides of the triangle. With 28 per cent of oxygen in the O_2 - N_2 -mixture the explosion region is much smaller; it is limited by the curve BDC and only one of the sides of the triangle. Mixtures of NH_3 and an atmosphere containing 28 per cent of oxygen are not inflammable. The explosion space, drawn in figure 23, contains a metastable part UVLKQW. There only supersaturated vapor could have been used. The experiments show that there is a regular decline from the top of the curve which limits the explosion region C_2H_5Br - O_2 - N_2 to that which limits the explosion region NH_3 - O_2 - N_2 .

It would be interesting to find a space figure in which a horizontal section shows an explosion region which does not reach a side of the triangle. That is to say the case that the explosion region BDC of figure 24 has contracted to a region surrounded by a closed curve (36).

Another case of four gases or vapors will be treated here, *viz.*, methane-air-carbon dioxide-carbon tetrachloride vapor (37). This system has been investigated (as part of a systematic research on the prevention of mine explosions), in order to test the possibility that two inhibitors will produce an enhanced effect, when working together, so that prevention will be attained with a smaller percentage of the two together than with either separately.

The damping possibilities of carbon dioxide on methane-air explosions had already been investigated by H. F. Coward and Hartwell (38). They found that the explosion limits coincided with 25 per cent CO_2 . Previous to this, experiments had been carried out in this direction by P. Eitner (11), J. K. Clement (39) and G. A. Burrell and G. G. Oberfell (40) by partially replacing the oxygen of the air with CO_2 . Clement (39) also determined the damping action of carbon dioxide in mixtures of air and natural gas (83.1 per cent CH_4 , 16.0 per cent C_2H_6 , 0.9 per cent

N₂). He found in a Hempel burette, that the explosion limits coincided with 20.5 per cent CO₂.

The influence of carbon tetrachloride on the explosion limits of methane in air has been studied by ourselves (41) and, under different conditions, by H. F. Coward and G. W. Jones (21).

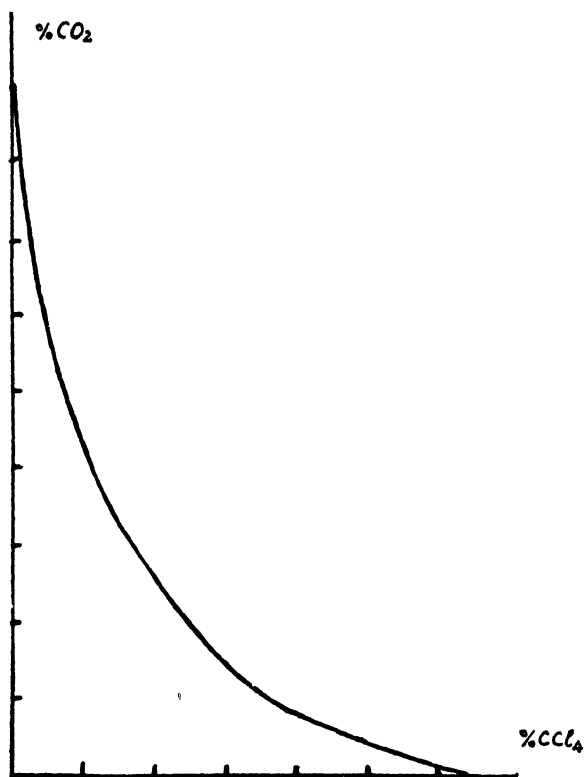


FIG. 25. VERTICAL SECTION OF THE EXPLOSION SPACE CH₄-air-CCl₄-CO₂

If it had been our purpose to make a complete study of the quaternary explosion region methane-air-carbon dioxide-carbon tetrachloride vapor, we might after determining the ternary region methane-air-carbon tetrachloride vapor, have investigated the alteration of the latter produced by the addition of carbon dioxide. The carbon dioxide contents could then have been

measured on an axis perpendicular to a triangle representing the ternary region.

For the sake of simplicity, however, we investigated only a vertical section through the explosion body, that is, we considered a plane, perpendicular to the triangle and passing through the CCl_4 corner and through the point on the opposite side of the triangle representing 9 per cent methane (this being one of the most highly explosive of such mixtures).

The section of the explosion body in this plane thus appears as a curve between rectangular coördinates, the horizontal axis being the CCl_4 axis and the vertical the CO_2 axis, the origin

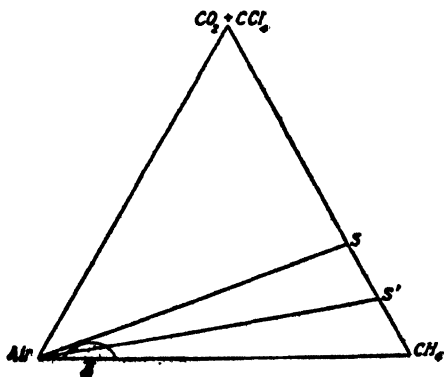


FIG. 26

representing the methane-air mixture. In order to make this mixture non-explosive 9 per cent CO_2 or 6.4 per cent CCl_4 was necessary (in our explosion buret). The section is shown in figure 25. As may be seen from this graph, the two inhibitors have a fairly strong influence on one another. The figure shows that, for instance, 1.8 per cent CCl_4 and 2.7 per cent CO_2 , or 4.5 per cent of a mixture of CO_2 and CCl_4 vapor containing 40 per cent of the latter substance, is necessary to make the methane-air mixture non-explosive. In a mine more than 4.5 per cent would be necessary, as the explosion region would be greater (less loss of heat to the surroundings, the possibility of upwards propagation, of more intense ignition, etc.). As 40 per cent

CCl_4 is a greater content than corresponds to carbon dioxide saturated with CCl_4 vapor, the mixture would have to be added

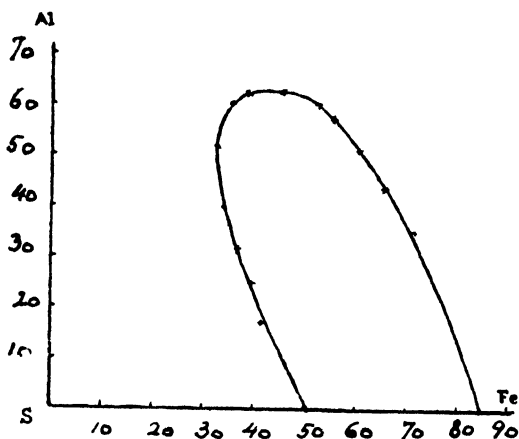


FIG. 27. REACTION REGION Fe-Al-S

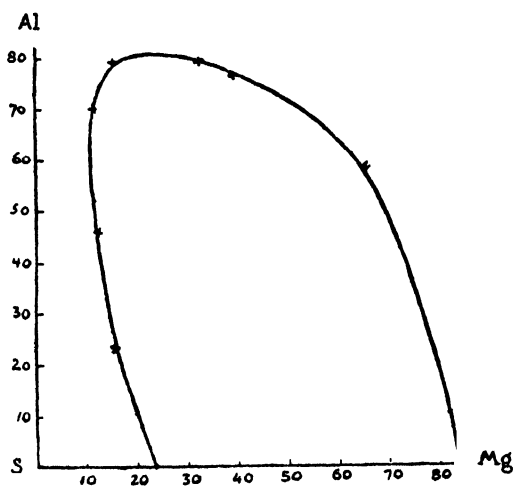


FIG. 28. REACTION REGION Mg-Al-S

in the form of a CCl_4 spray by means of a cylinder of liquid carbon dioxide.

Let E represent in figure 26 the explosion region of methane with air and a certain mixture of CO_2 and CCl_4 . Now if such a mixture is introduced into a pocket of mine gas and if the composition of the $\text{CH}_4\text{-CO}_2\text{-CCl}_4$ mixture obtained be represented by S, then, if the line S-air lies outside the explosion region, an explosive mixture will never be obtained on ventilating with air. An explosive mixture would, however, be obtained if the composition were represented by S'.

In practice the amount of CO_2 and CCl_4 required will not be known. However, in general the spraying of CCl_4 with liquid CO_2 might be of service as a fire extinguisher and, in some cases, could be applied to prevent the occurrence of explosions.

It still remains desirable to find a *harmless* substance, or mixture of such substances, which used in *small quantities* will exert a complete retarding action on methane explosions. A systematic research in this direction is being made in our laboratory.

B. Till now only two *reaction spaces* have been investigated using four solid substances.

In the first place a simple system was chosen, *viz.*, Fe-Mg-Al-S (42). The reaction region Fe-Al-S and Mg-Al-S are drawn in figures 27 and 28.

Let us now look at figure 29. In the triangle Mg-Fe-S we see the reaction region JKLH of those elements, J and H being the reaction limits of Mg with S, K and L the reaction limits of Fe with S. We now add Al and measure its quantity upwards along parallel lines, which are at right angles to the plane of the triangle. The reaction limits Mg-S and Fe-S will approach each other and coincide at certain percentages of Al. The horizontal projections of the tops of the two curves lie at G and F respectively. The upper part of the figure must be imagined to be folded at the line Mg-Fe and used as a vertical projection. Thus the vertical projections of the two tops mentioned above lie at A and E respectively.

If we now use mixtures of Mg and Fe (containing 75 per cent Mg, 50 per cent Mg or 30 per cent Mg) instead of Mg or Fe alone, we get curves whose tops have B, C and D as vertical

sulfur, representation in a regular tetrahedron would be preferable. This case would have occurred if the circumstances of the experiment had been of such a nature that the aluminium and sulfur had shown reaction limits.

The second system studied (ammonium dichromate-sulfur-iron-silica) was a continuation of that described on page 31. In the region represented in figure 22 a narrowing at HK occurs. This opened the possibility that on the addition of a deadening substance, such as silica, the region would split into two regions.

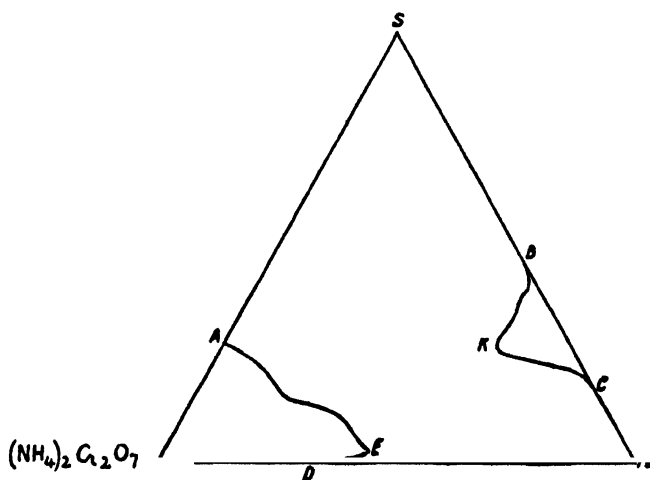


FIG. 30. HORIZONTAL SECTION THROUGH THE REACTION SPACE $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ —Fe—S— SiO_2 (12 PER CENT SILICA)

Therefore a horizontal section was investigated through the quaternary space, which is obtained when the quantities of silica are set out vertically, starting from the plane of the region $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ -S-Fe. As about 9.5 per cent silica appeared to make H and K coincide, a section was taken at 12 per cent silica in order to be sufficiently above the place of coincidence. The results of the experiments (8) are represented in figure 30. The two regions into which that in figure 22 has divided already lie fairly far apart. The projection E is still present in the left hand region.

This short review of what has been investigated in the domain of reaction limits, reaction regions and reaction spaces shows what has been achieved so far and part of what remains to be done. In every direction there is a fair chance of discovering interesting facts.

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THE GEOCHEMISTRY OF IODINE AND ITS CIRCULATION IN NATURE¹

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Since iodine was discovered by Courtois in 1811 the question of its occurrence and distribution in nature has been the subject of much research. In the older literature we find that a number of scientists claim to have found iodine in the majority of materials examined. The French pharmacologist, A. Chatin was especially interested in the question of the occurrence of iodine. In a number of works which were published about 1850, and afterwards, he established and demonstrated the presence of iodine in plants and animals, and in air, water and soil. He found this element everywhere, but in very small quantities. It appeared that all the iodine in the world was distributed everywhere, and that thus it was everywhere to be found only in very small concentrations.

I must not omit to mention another French scientist A. Gautier, who about 1900 published the results of his investigations on the occurrence of iodine in sea and air. Through him we find also the first mention of the occurrence of iodine in igneous rocks. He was the first, who with certainty demonstrated and established this fact.

Contemporary scientists doubted the correctness of Chatin's investigations however, and a committee, appointed by the Academy of Sciences in Paris to verify his results could only partly confirm their correctness on account of the defective analytical methods at their disposal.

Later investigations of the occurrence of iodine, however, showed that Chatin's results were quite correct. The Swiss

¹ Presented at the Second Session of The Institute of Chemistry of the American Chemical Society, Evanston, Illinois, July 24, 1928.

Scientist, Th. von Fellenberg, also investigated the whole of nature, organic and inorganic, and in agreement with Chatin was everywhere able to demonstrate and determine quantitatively the occurrence of iodine in small quantities. The impression we get of the occurrence and distribution of iodine from these authors is thus almost as follows: Iodine seems to occur everywhere, in rocks, in the sea, in the air and in all organisms. But no conformity to law in regard to its occurrence and distribution was demonstrated. We note specially that iodine is always present in organisms. There is also comparatively more iodine in plants than in animals. Whence comes this iodine in organisms? Where was the iodine before the birth of organic life, when the earth was still a floating mass? In other words, it is the history of iodine that we wish to clear up.

The questions regarding the history of elements and the laws affecting their distribution on earth are the subjects with which the new modern branch of science, geochemistry, is concerned. The first object of geochemistry is to find out the laws for the distribution of the elements on the solidification of the earth. This branch of geochemistry has been specially worked out by V. M. Goldschmidt and H. S. Washington. As the earth cooled and organic life began, a whole range of elements were drawn into the organic world. Such elements as chiefly build up organisms are carbon, hydrogen, oxygen, nitrogen and a number of others, but also the great majority of the other elements are regularly found, in greater or lesser quantities, as component parts of organisms. The branch of geochemistry, which specially includes the history of the elements in the organic circulation, we can call bio-geochemistry and this has been particularly worked out by the Russian scientist W. Vernadsky.

We shall now first discuss the geochemistry of iodine, its history and its laws of distribution. I follow here the views propounded by V. M. Goldschmidt as to the geochemical distribution of the elements, according to which the chemical components of the earth, on solidifying, divided themselves, according to affinity and specific weight, into several concentric shells or phases. The innermost is a kernel, consisting of metallic iron; outside

this a sulfide phase, chiefly consisting of ferrous sulfide and, outside all, a molten silicate mass, whose outermost layer forms the crust of the earth. Besides these fluid phases we had a steam-phase that now forms the atmosphere and the hydrosphere. I cannot here go further into these interesting matters, but they have been published by V. M. Goldschmidt in a series of papers in "Skifter utgitt av Videnskapsakademiet i Oslo." Goldschmidt has sought to find distribution laws for the chemical elements, and he has characterized the elements which are found concentrated in the iron kernel as siderophile, those that are concentrated in the sulfide shell as chalcophile, and those that are concentrated in the silicate mass as lithophile, and finally he called the elements that are present in the steam-phase, the atmophile.

In which of these phases was the iodine or the main portion of the iodine at the time of the earth's original separation into phases? In order to answer this question it was necessary to examine the various phases as to their iodine-content.

That we today find iodine in the air and in the sea, that is in the atmosphere and in the hydrosphere, is no proof that there was iodine in the original steam-phase. It may have come there later on. This question might be settled by systematically determining the ratio between the quantity of chlorine and iodine in the igneous and the sedimentary rocks. Should the sedimentary rocks contain more iodine in proportion to chlorine than the igneous, then we could conclude that iodine must have occurred in the original steam-phase, and thus become a constituent part of the first hydrosphere.

Such investigations have not yet been carried out, but we shall subsequently see that we have been able in another manner to give a positive answer to this question. We note in the meantime that iodine is found in the atmosphere, and that therefore according to Goldschmidt's nomenclature, it shows atmophile characteristics.

The next question will be: Does iodine occur also in the other phases, for instance in the silicate mass, the lithosphere. In order to answer this, von Fellenberg of Bern and I have together

conducted a series of experiments to determine the iodine content of igneous rocks.

The result of these investigations is, in short, the following: Iodine could be demonstrated and quantitatively determined in all the igneous rocks examined. I cannot here go further into the

TABLE 1
Iodine content of igneous rocks and minerals

	<i>mgm. per kgm.</i>
<i>Rocks:</i>	
Granite, Fredrikshald	0 20
Larvicite, Larvik	0 30
Labradorite, Ekersund	0 23
Obsidian, Island	0 32
Basalt, Daltenberg, Siebengebirge	0.31
<i>Minerals:</i>	
Marble, Carrara ..	0 55
Marble, Velfjord, Nordland	0 07
Titanite, Blåfjell, Ekersund ..	0 77
Hypersthene, Soggendal, Ekersund-Territory ..	0 94
Labradorite, Soggendal, Ekersund-Territory ..	0 44
Biotite, Kragerø	0 50
Hornblende, Kragerø	0 16
Scapolite, Risør ..	0 23
Sodalite, Brevik	0 90
Phlogopite, Bamle, Ødegården ..	0 63
Apatite, yellow, Bamle, Ødegården ..	0 18
Perithitic-microcline, Halvorsrød, Råde, Østfold ..	0 37
Albite, Halvorsrød, Råde, Østfold ..	0 15
Muscovite, Halvorsrød, Råde, Østfold ..	0 69
Fluorspar, Halvorsrød, Råde, Østfold ..	0 55
Smoky Quartz, Halvorsrød, Råde, Østfold ..	0 33

methods used in determining these small quantities, but will only refer to the bibliography.

The quantity we find is about 0.2 to 0.3 mgm. per kilogram. All igneous rocks appear to contain the same quantity, or at any rate quantities of the same order. Nor can we find any difference in the iodine content in the more basic and the more acid

rocks. In table 1, I have grouped some figures that illustrate this.

It might now be of interest to know if the iodine content in the rocks was united to a certain mineral or if it was evenly divided over the whole mass. In order to investigate this, a number of rock-forming minerals were examined as to their iodine content, and we find it noteworthy that all minerals, with some few exceptions, contain more iodine per kilogram than the rocks. (See table 1.) This fact is however, easily explained. For these investigations only large crystals were used, and these were probably all of them from pegmatitic veins. In the residual liquor of the magmatic differentiation out of which the pegmatitic minerals are crystallized, the easily soluble compounds are enriched, and as the alkali iodides belong to these easily soluble salts, we can expect to find an enrichment of iodine in just these minerals. The iodine has not, however, preferred any special mineral, if we except the fact that we find in mica minerals a fairly constant quantity of 0.6 to 0.7 mgm. iodine per kilogram. A number of minerals containing chlorine were examined, as it might be supposed that the iodine accompanied the other halogens, but this proved not to be the case. Some of the minerals were tested also as to their bromine content, but the proportion between bromine and iodine content was variable and without any distinct conformity to law.

That iodine besides its atmophile tendencies, has also a lithophile character is thus confirmed, but we know nothing as yet of the laws relating to its distribution among the various minerals.

In order to test whether iodine, besides its atmophile and lithophile characteristics, also is capable of appearing in the other phases, von Fellenberg, at the suggestion of Professor Goldschmidt tested some magmatic sulfides as to their iodine content. These also are iodine-bearing, but they contain still smaller quantities than the silicates. We arrive therefore at the interesting result that iodine displays also certain chalcophile tendencies.

But we may ask, when iodine is found in all these three phases, why then is it not to be found also in the iron kernel of the earth? At first it appears quite out of the question that iodine should be

found in some form or other dissolved in the iron, but our investigations have proved that this really is the case. If iodine is found in the earth's kernel, it must in some way or other be soluble in iron, and as iodine is found in all materials that are used in iron smelting works, we might expect to find iodine in all technical

TABLE 2
Iodine content of various irons and steels

NUMBER	MARK	ORIGIN	IODINE <i>mgm. per kgm.</i>
1	Hematite	Germany	0 35
2	Hematite	Luxemburg	0.10
3	Hematite	Luxemburg	0 18
4	Hematite	France	0 28
5	Hematite	Longwy	0 69
6	Hematite	Holland	0 50
7	Hematite	England	0 28
8	Grey cast iron	Geneva	0 43
9	Wrought iron	Geneva	0 62
10	Electro steel	Geneva	0 40
11	Cast steel	Geneva	0 55
12	Steely iron	Switzerland	0 22
13	Steel 8N ₂ C ₂	Sweden	0 25
14	Steel Ti ₃ W	Tcheckoslovakya	0 38
15	Steel 3Ni ₃	Sweden	0 70
16	Steel CNS	Tcheckoslovakya	0 25
17	Steel S ₁₀	Sweden	0 40
18	Steel 1Ni ₃₀	Switzerland	0 70
19	Steel 3Ni ₃₀	Switzerland	0 31
20	Steel 1Ni ₄₀ Cr ₁₀	Switzerland	0 26
21	Steel M ₄₀	Germany	0 26
22	Steel C ₁	Switzerland	0 63
23	Steel E 60/70	Switzerland	0 17
24	Nave steel	Germany	0 19
25	Nave steel E ₂	Germany	0 56
26	Nave steel E ₄₅	Germany	1.10

iron. In the smelting of iron, coke is used, an article which is particularly rich in iodine, and an admixture of lime, which is also generally rich in iodine. All the conditions favorable to such a result are thus present.

Following up this idea, von Fellenberg and I set to work to test

a number of varieties of technical iron and steel as to their iodine content. We examined, in all, 26 different specimens and found in all of them iodine varying from 0.1 up to 1.1 mgm. iodine per kilogram of iron.

We found, however, no relation between the iodine content, and the chemical composition of the iron. The quantity of iodine present in the iron is dependent only on the iodine content of the materials used in the working of it.

It was now proved that iodine is a constant associate of all iron, but still it was not proved that iodine appears in the earth's iron kernel, though our investigations showed that it was very probable.

A proof of the siderophile character of iodine was however forthcoming when von Fellenberg succeeded in determining iodine in iron-meteorites. The iodine content in the iron-meteorites tested, varied from 0.14 to 1.5 mgm. per kilogram. As we must assume that meteorites come from heavenly bodies that have approximately the same chemical composition as our own planet, we may take it for granted that iodine must also be found in the earth's iron phase, and thus is also siderophile.

Regarding the concentration of iodine in the earth's iron kernel, however, we still know nothing. The meteorites examined give, of course, an indication of the order of size, but we can come to no certain conclusion. On the original division of the earth into phases iodine must however, have been distributed between the various molten masses according to its affinity to every single one of them, and there must be found a proportion for this distribution, conformable to a fixed law. This proportion von Fellenberg endeavored to obtain by testing the proportion between iodine concentration in the two different phases in a so-called compound-meteorite, which contains both iron and a solidified silicate molten mass separated from this. In the case of a compound meteorite from Bomba there was found a distribution quotient between silicate and iron of 100:15. There was, however, as von Fellenberg personally has informed me so little material for such a test that these figures cannot form any basis for broader conclusions.

I accordingly endeavored to find the distribution quotient in another manner. We have seen that iodine is found in all varieties of technical iron. It is therefore natural to suppose that iodine must also occur in the slag formed in iron smelting. In the technical blast furnaces we find, however, both the fluid iron mass and the fluid silicate slag present at the same time, and the iodine will be distributed according to its affinity between the two fluid phases. The distribution quotient between iron and silicate molten mass can thus be found directly.

TABLE 3
Analysis of iron furnace slags

A: Blast furnace slag, Steiermark, Austria.

B: Blast furnace slag, Choindez, Berner Jura, Switzerland.

C: Cupola furnace slag, Geneva, Switzerland.

	A	B	C
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
SiO ₂	36 47	32 71	56 14
TiO ₂	0 35	0 45	1 95
FeO	0 42	0 63	7 95
Al ₂ O ₃	9 00	12 83	15 16
MnO.....	6.43	1 90	4 57
MgO.....	15 16	1 00	0 87
CaO.....	29 39	48 93	12 78
S	1 03	0 57	0 03
Sum	98 25	99 02	99 39
— O for S.	—0 52	0.28	0 01
	97 73	98 74	99 38

In pursuance of this idea I started an investigation of blast-furnace slags and iron, with the object of determining their iodine content. So as to be able to make a direct comparison with the crust of the earth the slags were analyzed.

Tables 3 and 4 show the iodine content of the slags and of the iron. We see that the proportion is about 100:50 or 2:1. The composition of these slags is, however, not identical with the composition of the earth's crust, nor with that of any existing rocks. In the first place these blast-furnace slags do not contain alkalis; likewise their calcium content in proportion to the mag-

nesium is generally greater than in rocks. They are also more basic than the average composition of all igneous rocks. We therefore tested a cupola furnace slag and the cast iron obtained from it at the same time. This slag is considerably richer in silicic acid, and here we find the proportion somewhat displaced in favor of the iodine content of the iron. The order of magnitude is, however, the same, and as we know that the iodine content of silicate rocks is 0.2 to 0.3 mgm. per kilogram, we can place the iodine content of the iron kernel at 0.1 to 0.15 mgm. per kilogram.

Our studies in connection with the blast-furnace process made another matter clear for us. In the dust which was found left in the flue, the iodine was many times enriched as compared with the content in the slag and in the raw materials used. From this

TABLE 4
Iodine content of slag and of corresponding iron

	IODINE		PROPORTION
	Slag	Iron	
	mgm. per kgm.	mgm. per kgm.	
A	0 80	0 32	100:40
B	0 85	0 32	100:59
C	0 60	0 43	100:72

we may conclude that the iodine escaped in its elementary form during the process and was caught by the particles of dust in the flue. Von Fellenberg had also previously found a high concentration of iodine in fireplace-soot and also in cement dust. We have thus the direct proofs also of the atmophile character of iodine. We can sum up the results arrived at in the following law regarding the geochemical distribution of iodine: *Iodine is an element, as far as we hitherto know the only one, which on the earth's division into phases did not show remarkable affinity to any of the phases. It became part of them all, but showed, however, more conspicuous atmophile and lithophile than chalcophile and siderophile characteristics.*

Besides the four inorganic phases into which Goldschmidt divides the earth in his geochemical survey, we have still a fifth

one, the biosphere. The biosphere is bounded by the atmosphere and the hydrosphere on the one side, and the rocks on the other, and is the seat of all the organic life on earth. As I have already mentioned it was Vernadsky in particular, who urged the importance of the biosphere in all geochemical surveys.

When an element enters into organisms and is thus drawn into the biosphere, its geochemical history is changed in an essential degree. Iodine is in this case specially interesting because the concentrations in which most often we find it in the biosphere are greater than in the rocks. A concentration of iodine must therefore have taken place in the biosphere. Iodine has, so to speak, been pursued by organisms.

Another characteristic of iodine is that it is found in specific combinations with other elements, and this also only in the biosphere. The iodine minerals that we know are formed and exist only in the upper layers of the earth's crust, and only in deposits of organic origin. These minerals are, however, all of them, relatively rare. We must assume that the iodine content here has been enriched by organisms capable of accumulating iodine and that through the decay of these organisms it was withdrawn from the organic circulation. We know the compounds iodargyrite, AgI , marshite, CuI , and miersite, $4\text{AgI} \cdot \text{CuI}$. This last must be regarded as a mixed crystal of AgI and CuI . Further, we know iodembolite $\text{Ag}(\text{Br}, \text{I})$, a mixed crystal of AgBr and AgI . In the saltpeter deposits in Chile we find the minerals lautarite, $\text{Ca}(\text{IO}_3)_2$, and dietzeite, $7\text{Ca}(\text{IO}_3)_2 \cdot 8\text{CaCrO}_4$. All these, however, except the silver minerals are mineralogical rarities. We cannot say this of the occurrence of iodine in the saltpeter deposits above mentioned, for there we find iodine in very great quantities. The annual production in Chile is about 70 per cent of the total world production, nevertheless only 10 per cent of the total iodine content of the minerals is utilized as iodine. Nevertheless these great quantities of iodine are practically negligible compared with the enormous reserve of iodine in the rocks.

When the earth cooled, the first steam-atmosphere was condensed and became the hydrosphere and an atmosphere which

contained less moisture. Disintegration of the rocks took place, and in consequence part of the iodine which was found in the rocks was released. The greater part of the iodine of the disintegrating rocks accompanies them when they become soil. Plants take their iodine from the soils, animals get their iodine by feeding on plants. Figure 1 shows the circulation of iodine in nature. Plants and animals on decaying set free their iodine again. But plants do not obtain their iodine exclusively from the soil; they also absorb iodine direct from the atmosphere. They "inhale" iodine. When they decay, a good deal of the iodine set free escapes again into the air. During certain processes some iodine is set free from the soil and escapes into the atmosphere. The atmosphere returns iodine to the soil again; the

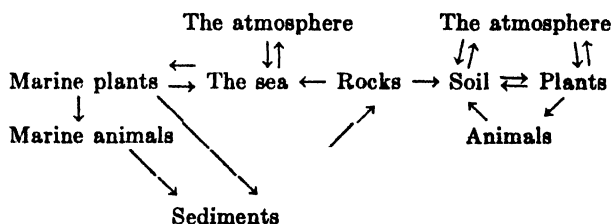


FIG. 1. CIRCULATION OF IODINE IN NATURE

iodine falls to the earth dissolved in rain-water. Also snow, hail and rain etc., contain iodine. Plants are always richer in iodine than animals.

A part of the iodine which is set free by disintegration is carried away by surface water. Fresh-water algæ absorb great quantities of iodine and are considerably richer in iodine than land-plants. Fresh-water fish again get their iodine from these algæ.

The iodine which is not captured by organisms is carried by the surface water into rivers and thus into the sea. The sea has obtained its iodine-content, partly in this way, and partly from the first steam-atmosphere which surrounded the earth. The iodine concentration in the sea is considerably greater than in fresh water. Many scientists have fixed this at about 0.02 mgm. per liter. Marine algæ are therefore also richer in iodine than

fresh-water plants and for the same reason marine animals are also richer in iodine than land-animals and freshwater ones. Figure 1 shows how plants obtain iodine from the sea, sea-animals again from plants. On the decay of organisms a part of the iodine is again set free, but large quantities are withdrawn from the organic circulation and pass over into sediments. In later geological periods, these sediments may be forced up above the sea-level, they may again be exposed to disintegration and the iodine be set free. It will then be drawn into the biosphere, and

TABLE 5
Average iodine content of the most common Norwegian teleosts

	IODINE	
	Moist	Waterfree substance
	mgm. per kgm.	mgm. per kgm.
<i>Gadus aeglefinus</i> (Haddock).....	6 23	29 34
<i>Gadus morrhua</i> (Cod) ..	5 17	24 55
<i>Brosimius brosme</i> (Cusk).....	3 60	17 85
<i>Molva molva</i> (Ling).....	3 11	14 98
<i>Gadus virens</i> (Pollock) ..	2 65	13 37
<i>Sebastes marinus</i> (Red-fish).....	1 41	6 60
<i>Hippoglossus hippoglossus</i> (Halibut).....	1 19	4 59
<i>Pleuronectes platessa</i> (Flounder).....	0 71	3 61
<i>Scomber scombrus</i> (Mackerel).....	0 45	1.75
<i>Salmo eriox</i> (Sea-trout).....	0 37	0 90
<i>Clupea harengus</i> (Herring).....	0 17	(0 52)
<i>Salmo salar</i> (Salmon) . . .	0 26	0 50

we have the iodine circulation completed. In these remarks regarding the circulation of iodine I have chiefly confined myself to publications by von Fellenberg and myself, but I must not fail to call attention to important papers by J. F. McClendon on the iodine content in various fresh waters in the United States and weighty investigations of the iodine content of various foodstuffs from goiterous and non-goiterous regions in the United States.

During the past year I have made a special study of the iodine content of marine organisms, for the purpose of making clear the circulation of iodine in the sea. As far as the iodine content in sea-organisms is concerned, if we omit the determinations

governing iodine content in marine algæ, we have only some older investigations on fishes by the French scientist, P. Bourcet, as well as more recent investigations by D. K. Tressler and A. W. Wells of the United States Bureau of Fisheries in Washington.

In coöperation with Karl Closs, Helmer Haaland and Sigurd Opstad Madsen, some representatives of the commonest Norwegian teleosts were examined. The results are to be found in table 5.

Compared with the figures found by Bourcet, Tressler and Wells, our own are much higher. It is therefore probable that the iodine content is dependent on the location of the fishing grounds.

TABLE 6

Iodine content of the intestinal canal of Norwegian teleosts

	IODINE IN WATERFREE SUBSTANCE	
	Muscles	Intestinal canal
	mgm. per kgm.	mgm. per kgm.
<i>Gadus aeglefinus</i> (Haddock)	29.4	42.3
<i>Gadus morrhua</i> (Cod)	24.6	41.8
<i>Scomber scombrus</i> (Mackerel)	1.75	1.40
<i>Salmo eriox</i> (Sea trout)	0.90	4.08
<i>Salmo salar</i> (Salmon) ..	0.50	1.65
<i>Clupea harengus</i> (Herring)	0.60	2.24

The specimens examined by us were caught in spring 1928, at Moere on the west coast of Norway.

The great difference in the iodine contents of the flesh of the species examined made it appear probable that the iodine content of the flesh depended on the character of the food. In order to prove this the intestinal canal of some of the most typical species were examined. The result of these investigations which are shown in table 6, show that the teleosts with the high iodine content of the flesh also always show a very high iodine content of the intestinal canal. The iodine-poor fishes, however, always give much smaller figures for the iodine content of the intestinal canal. Another interesting fact is that the species of teleosts which we found to be rich in iodine always are poor in fat and

rich in phosphorus. We further see that fishes rich in iodine are what we can call typical bottom fishes which chiefly feed on invertebrates of the bottom fauna. In collaboration with Closs and Madsen some typical specimens of the bottom fauna were examined, and in accordance with our supposition we found large quantities of iodine. Table 7 gives a review of some of our results.

Table 7 contains our results for the invertebrates examined. In order to get a complete picture of the cycle of iodine in the sea, it was, however, first necessary to examine the plankton. The lower types of sea-animals and a great number of fish derive their chief supply of food from plankton.

TABLE 7
Iodine content of some invertebrates of the bottom-fauna

	IODINE IN MOIST (FRESH) SUBSTANCE
	<i>mgm. per kgm.</i>
Actinia	1 0-4 7
Ascidians	33 0
Asterias	1 1
Culcita pentangularis	15 3
Holothurian, Stichopus	1 0-3 3
Muschel, indetermin	6 9
Octopus	8 4
Pandalus (Norwegian shrimp)	5 1

In coöperation with Karl Closs, I examined a large supply of phytoplankton, chiefly consisting of diatoms taken from the Oslo Fjord in March. The moist plankton contained 38.09 mgm. of iodine per kilogram, or 230.91 mgm. per kilogram water-free substance, that is not only a larger quantity than in all other organisms previously investigated, but also of a quite different order of magnitude. The iodine content determined, is of a like order of magnitude as the iodine content in the various species of sea-weed (*Fucus*, *Laminaria*).

The plankton is thus able to concentrate the marine iodine. The iodine content of the ocean is about 0.02 mgm. per liter. Various scientists have arrived at various values; the quantity

appears also to vary greatly with the locality, but the order of magnitude is always the same. According to von Fellenberg's investigations up to 25 per cent of this iodine is united to insoluble filterable particles (plankton). It is clear that these figures must vary considerably as the production of plankton for many reasons may be very great or very small. We see, however, that iodine is about 10,000 times as concentrated in water-free plankton as in the sea water. This gives a good idea of the extent to which plankton is capable of concentrating iodine. Samples of zooplankton also were examined and were found to be rich in iodine. Thus we found for the most common crustaceans the figures given in table 8.

TABLE 8
Iodine content of crustaceans

	IODINE IN WATER-FREE SUBSTANCE
	<i>mgm. per kgm.</i>
Red copepods (<i>Calanus finmarchicus</i>)	11.6-21 9
Schizopods (<i>Meganocytiphanes norvegica</i>)	7.1
Amphipods (<i>Euthemisto compressa</i> et <i>E. bispinosa</i>)	13 0

On the basis of the investigations which we now have at our disposal we can form an idea of the circulation of iodine in the sea, or in other words the iodine metabolism of the sea, roughly as follows: (see fig. 2). The iodine that is released from weathered rocks is carried by the rivers out to sea. Here it is absorbed by the plankton just like other nutritive salts from the land (especially phosphorus and calcium compounds). The production of plankton is periodical and depends at the Norwegian coast chiefly on the supply of nutriments from land. It is especially rich during the melting of snow in spring; at that time the great quantities of iodine, which have been released by the erosion of rocks in the course of the winter, are carried more or less suddenly out into the sea. During and immediately after the flowering of plankton in the upper layers of the ocean, only a very small quantity of it is utilized as food for the lower or higher species of animals (especially zooplankton). The great mass

sinks to the bottom, and some of this plankton serves there as food for the invertebrates of the bottom fauna. The bottom fishes, as we have seen before, obtain their iodine mostly from these animals. On the decay of the various plants and animals a part of iodine is, as mentioned before, once more set free and can then be absorbed anew by plants. But large quantities of iodine are withdrawn from the circulation by the fact that they sink to the bottom with the remains of plants and animals and pass over into the sediments.

There is also a constant reciprocal action between the surface of the sea and the atmosphere. By certain processes iodine is

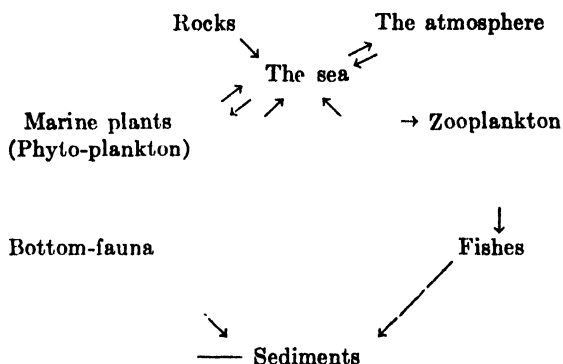


FIG. 2. CIRCULATION OF IODINE IN THE SEA

set free at the surface, it escapes and passes over into the atmosphere. It is carried back into the sea again by precipitation. As the concentration of iodine in the sea is so much higher than in fresh water, it is clear that sea-air will be considerably richer in iodine than inland air. And this fact is of no little importance for both men and animals in districts along the sea-coast. For experiments have shown a higher concentration of iodine in the surrounding nature and therefore in all organisms in coastal districts compared with corresponding inland organisms.

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PROBLEMS IN THE CHEMISTRY OF COAL¹

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This lecture will deal with the major problems in the chemistry of coal, taking up first its constitution and formation, passing thence to a discussion of other problems in coal chemistry and their bearing upon a chemical industry based upon coal.

From microscopic studies of coal and observations of the processes of decomposition and transformation which occur in decayed organisms in nature, we obtain a clue to the basic substances in the formation of coal. Such studies teach us that coal was formed from the lignified portions of higher plants, pollens, spores and the flora and fauna of plankton, or, chemically speaking, from woody substances, fats, albumins, resins, and waxes. We differentiate these coals as *humus coal* and *sapropel coal*, depending on whether the raw material from which they were produced was wood or a material rich in fats and albumin. Often both forms occur in alternate layers. So-called striated coal is well-known, i.e. a hard coal made up of bright coal, called *humus coal*; and dull coal called *sapropel coal*, with a kind of mineral charcoal called *mother of coal*. Recently Stopes and Wheeler have introduced the nomenclature *Clarain* for the bright coal, *Durain* for the dull coal, and *Fusain* for the mother of coal. According to Thiessen of the Bureau of Mines what was originally called *Vitrain* by them and was said to have no structure does actually possess structure and is identical with *Clarain*. Thiessen calls *Clarain*, which has a predominantly woody structure, *anthraxylon*, and *Durain*, which is a mixture of different materials, he calls *atritus*.

¹ An address given at the First Session of the Institute of Chemistry of the American Chemical Society, State College, Pennsylvania, July 15, 1927. The author is now Director of the Coal Research Institute, Prague VIII, Czechoslovakia. This manuscript was translated by Marion L. Kenney.

Little or nothing is known of the chemical structure of sapropel coal; consequently my remarks will be confined chiefly to the humus coals which are much more abundant than the sapropel coals.

According to Fuchs the woody substance of the kinds of coal-forming plants which have been studied show the same composition, qualitatively, at least, i.e. they consist essentially of cellulose and varieties of lignins. This warrants the certain conclusion that the substances in question participated in the formation of coal throughout all geological epochs. Consequently hard coals and brown coals are not, as was assumed for a time, fundamentally different formations conditioned by the difference in their raw materials, but rather represent different stages of a transformation process starting in the decayed plants. Of course it should not be maintained that our hard coals of today were once exactly like the brown coal of today. The degree of similarity existing between them would vary on account of the fact that the raw materials were not quantitatively, but merely qualitatively alike.

The organic material in humus coal consists essentially of the actual humus, forming the substance of the coal, and the bitumen. These two constituents can be separated by various solvents. Benzol and pyridine should be mentioned particularly as useful when the intention is to make a thorough study of the bitumen instead of limiting the study to a determination of the yields of the extraction.

Three characteristic stages are to be distinguished in the humus substance. Peat and the young brown coals have an acid character due to the presence of humic acids and dissolve in cold alkali with a dark coloration. This property is no longer found in the second stage represented by the older brown coals. The brown coal humins however, which are to be conceived of as anhydrides and lactones of humic acids can be dissolved by boiling in lye and so reconverted to humic acids. On the other hand, when heated to 250 degrees, humic acids are converted into the humins which are insoluble in alkali. The humus portion in hard coals, that is to say the third stage, is also insoluble in boiling alkali. However, according to Fischer and Schrader it can be converted into sub-

stances resembling humic acids by auto-oxidation at higher temperatures or by oxidation under pressure in the presence of alkali or by moderate oxidation with hydrogen peroxide. This indicates the genetic relation of hard coal humus to the humic acids and humins of brown coal from which the humus substance is formed as a result of a more extensive condensation and polymerization process, with carbon dioxide, and water, and probably methane also, splitting off.

The easy interconvertibility of the three characteristic stages of the humus substance is itself an indication that no fundamental alteration in the chemical structure can have taken place during the transitions of the humic acids first into humins and finally into the substance of hard coal. Fischer and Schrader have now shown that the decomposition of coal by pressure-oxidation with air in the presence of soda solution runs in the same way in all humus coals.

First there are obtained dark solutions of products similar to humic acids which, with progressive oxidation, are then broken down to lighter acids with smaller molecular weights. To be sure, it is not yet possible to isolate individual chemical acids from these but when the decomposition is carried further aromatic carboxylic acids and lower aliphatic acids are formed. Under pressure-oxidation one of the vegetable substances, lignin, behaves like the humus substances while the cellulose reacts quite differently. The conclusions with respect to the formation of coal which Fischer and Schrader have drawn on the basis of these discoveries are yet to be discussed. The fact that at least one-third of the unidentified acid mixture consists of benzol derivatives, can be demonstrated by the fact that it is convertible into aromatic carboxylic acids by heating under pressure, benzoic acid and isophthalic acid in particular being obtained in this way (table A).

Since there is a further destruction of the aromatic carboxylic acids under the conditions of pressure oxidation the yields obtained by Fischer and Schrader are to be considered minimum and there can be no doubt that coal is essentially aromatic in structure.

By the use of alkaline permanganate solution to break down the coal substance which had previously been freed from bitumen by extraction, Bone and Quarendon have reached similar conclusions within the last few years. They also obtained large quantities of acids, probably aromatic, which they were unable

TABLE A

Oxidation under pressure from cellulose, lignin, brown coal and bituminous coal

	VOLATILE ACIDS	NON- VOLATILE ACIDS	RECOGNIZED HITHERTO	
			Quantity	Acid
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	
Cellulose.	ca. 28	ca. 14	0.7	Fumaric
			5.0	Succinic Oxalic
Lignin.....	ca. 11	ca. 34	>0.3	Mellitic
			3.7	Benzene pentacarbon
			7.2	Oxalic
Brown coal.....	ca. 14	ca. 34		Mellitic
				Benzene pentacarbon
				Pyromellitic
				o-phthalic
				Benzoic
Bituminous coal....	Not estimated	ca. 30	0.58	Mellitic
				Benzene pentacarbon
			0.93	Trimesinic
			0.33	Phthalic
			0.35	i-phthalic
			11 after heating under pressure	Benzoic Benzoic and phthalic

to identify. Definite aromatic carboxylic acids, particularly mellitic acid, could however only be obtained in amounts equal to 0.8 to 1.6 per cent of the coal used.

Under pressure-oxidation, cellulose behaves quite differently from coal and lignin. No humic acids are formed as intermediate products and, when oxidation is pushed farther, large quantities

of aliphatic acids are obtained. In particular acetic acid, oxalic acid and small quantities of fumaric and succinic acids have been identified. On heating under pressure the non-volatile and unidentified acids yielded furan. It is noteworthy that, under the same conditions, no furan can be obtained from coal and lignin and consequently the old view as to the furan structure of coal has no justification. The detection of furan derivatives among the products of pressure-oxidation of cellulose proves also that the furan ring is fairly stable under this method of decomposition and that, if furan derivatives resulted from the pressure oxidation of coal, they would surely have been observed.

Not only is the aromatic structure of the humus portion of coal indicated by the results of the break-down by oxidation; it is confirmed also by the character of the products obtained from coal by Bergius and Billwiller on treating it with hydrogen under pressure at temperatures around 450 degrees.

Working with Ter-Nedden, I was able to show that, in addition to 20 per cent phenol, cyclic hydrocarbons were present in the products obtained by Fischer and Frey from the high pressure hydrogenation of lignite semi-coke. Kling and Florentin obtained benzol derivatives almost exclusively in the pressure-hydrogenation of hard coal from lower Silesia.

As we have seen, all decomposition reactions which have been undertaken with the humus substances of lignite and anthracite coal pass through the humic acids. On the other hand these represent a conversion product of plant substances in the process of decay. The humic acids therefore point the way to a better knowledge of the constitution and formation of coal. In many reactions the humic acids possess quite the character of phenol derivatives. Nitrophenol-like substances result on treatment with nitric acid. Schellenberg and I succeeded in isolating a quantity of a well crystallized trinitrodioxybenzol of unknown constitution, equal to 5 per cent of the humic acid used.

In recent years, Francis and Wheeler have likewise obtained nitrophenol-like substances, which they call regenerated ulmins, by the action of nitric acid on humic acids obtained from hard coal by moderate oxidation with hydrogen peroxide. Among

these nitrophenol-like substances they identified picric acid in a quantity equal to 2.7 per cent of the coal, a discovery which is somewhat like our own, and indicates that the humic acids regenerated from hard coal also possess a phenol structure. At this point it should be mentioned also that, as early as 1888, Guignet obtained from hard coal with nitric acid, a nitrophenol which he called trinitroresorcin. Many other reactions also indicate the phenolic character of humic acids.

The phenols of crude tar are to be traced back to the humin substances. On dry distillation to be sure, humic acids, isolated with admission of air, yield little or no tar. Erdmann, who isolated humic acids under particularly painstaking conditions, was however able to obtain from them, though only in small quantities, a tar which was very rich in phenol compared with the tar from the other constituents of coal. The products, still resembling humic acids, which are obtained after treatment of humic acids with lye at 300 degrees, also behave in this way.

An attempt was made to draw a conclusion as to the chemical constitution of humic acids from the formation of the artificial humic acids. It has long been known that alkali-soluble substances of the character of humic acids can be formed from various organic compounds. Best known are the artificial humic acids from carbohydrates, particularly from sugar. But humic acids should also be obtained from other classes of organic compounds. Easiest to convert into humic acids however are the higher phenols and phenol derivatives, such as pyrocatechol, hydroquinone, phenolcarboxylic acid, etc. This reaction which had long been known qualitatively was carefully studied by Eller and Koch. They have discovered a convenient way of preparing such synthetic humic acids in the oxidation of the phenols mentioned with alkali persulfate solution. If we examine the reactions which are known to lead to artificial humic acids we find that these run most smoothly from phenols. If we start with non-phenols, as for example from carbohydrates, an intermediate formation of phenols is possible directly; apparently therefore in the formation of the humic acids, it is a question of substances with phenol complexes. Here then we have genetic relations with one of the

constituents of the woody substance, lignin, which brings us to the question of the formation of the humic acids and then of coals in nature. Until a short time ago the view was held that cellulose was to be looked upon as the raw material of humic acids. This was even held to be almost an obvious conclusion since cellulose greatly preponderates in the substance of plants. The work of Hoppe-Seyler, Fremy etc., restricted mainly to biological fields, from which important conclusions as to the cellulose derivation of the humic acids can be drawn, were not very highly regarded by the chemists and geologists who worked with coal. In consequence of their discoveries in pressure-oxidation, Fischer and Schrader were the first to go deeply into the question of the plant constituent from which coal is formed and, on the basis of already known facts as well as their own experiments, they became convinced that genetic relations existed only between lignin and the humic acids and that, on account of its chemical and biological behavior, cellulose cannot be considered to take an essential part in the formation of humic acids.

The lignin theory of Fischer and Schrader states that, in the decay of plant residues, the cellulose is altered and consumed by the action of bacteria. It disappears with formation of carbon dioxide, methane, water, and water-soluble organic acids, such as formic acid, acetic acid etc., which are carried away by the water of the soil and may exert a solvent and decomposing action upon the rock beneath the peat. The quantity of aromatic lignin on the other hand increases with increasing age of the peat, going over to humic acids from which there then form the humus substances of brown coal which are insoluble in alkali and, finally, the substance of hard coal. The wax and resin-like materials of the plants remain however when the coal is formed and make up the bitumen.

Fischer and Schrader have adduced a large number of facts in support of their theory.

Though the chemical constitution of lignin cannot yet be cleared up entirely, we can now say with a reasonable degree of assurance that we have to do with a substance the molecule of which possesses an essentially aromatic and even phenolic

character. In various ways protocatechuic acid or derivatives of this acid, such as vanillic acid and eugenol can be obtained from lignin. Since aromatic carboxylic acids form from lignin under pressure-oxidation it is possible that unphenolated benzol rings are also present. Recently Fuchs has found an unsaturated sugar complex in the lignin molecule. All in all however, lignin, like the humic acids, may be considered to be of a phenolic character. This is shown for example in vacuum distillation which gives a tar very rich in phenol. The methoxyl content of lignin is important for the characteristic and easily recognizable methoxyl group makes it possible to trace the lignin in the formation of the coal. The genetic relations between lignin and the humic acids arise from their chemical similarity and the possibility of converting lignin into humic acids. This can be accomplished by heating with alkali liquors at 200 degrees or by auto-oxidation in the presence of alkali.

Interesting work, strongly supporting the Fischer-Schrader lignin theory, has been done in America. In 1917 Rose and Lisse, in an investigation of the decomposition of wood, showed that it goes hand in hand with a considerable decomposition of the cellulose, the lignin proving more resistant. Their figures for fresh, half decayed, and entirely decayed wood show that during the process of decay the relative content of methoxyl doubled, a proof of the increase in the store of lignin; the cellulose on the contrary disappeared. The studies of Rose and Lisse gave only relative values for lignin, cellulose etc. A new investigation by Bray and Andrews at the Forest Products Laboratory of Madison Wisconsin follows the decomposition of wood quantitatively.

Bray and Andrews started from weighed samples and made a systematic study of the biological decomposition. By a determination of the loss of weight they were able to establish not only the relative alteration but the absolute alteration of the individual constituents of the wood during the process of decay. The quantity of lignin, as indicated by the constituents insoluble in 72 per cent sulfuric acid, remains practically constant. In course of decay however the lignin becomes completely soluble in alkali and loses a part of its methoxyl content. On the other hand it can

be seen from the figures of Bray and Andrews (table B) that alkali-soluble and, to some extent water-soluble substances are formed from the cellulose which again disappears during the process of decay. The loss of weight suffered by the entirely decayed wood corresponds to the quantity of cellulose originally present. A splitting off of methoxyl occurs in the transition of the lignin into humic acids so that, in contrast to the lignin which in its most frequently occurring forms contains about 16 per cent of methoxyl, the humic acids show only a few per cent. The farther the carbon-

TABLE B
Chemical changes of wood during decay (Bray and Andrews)

STORAGE TIME	LOSS DUE TO DECAY	HOT WATER SOLUBLE	1 PER CENT ALKALI SOLUBLE	LIGNIN	CELLULOSE	PENTOSAN	METHOXYL
Based on equal weights of sample analyzed (figures in per cent)							
<i>months</i>							
0	0	1.2	10.1	29.7	60.0	12.0	5.5
6	27.12	17.95	54.9	38.0	36.7		
12	49.5	22.2	66.8	53.4	21.8		
36	62.4	16.5	70.0	71.0	16.1	6.8	7.2
Based on equal weights of original sample (figures in per cent)							
		1.2	10.1	29.7	60.0	12.0	5.5
		13.1	40.0	27.7	26.8		
		11.1	33.4	26.7	10.9		
		6.2	26.3	26.7	6.05	2.56	2.7

ization goes the more the methoxyl content shrinks so that, in hard coal, it is possible to detect no more than traces of methoxyl. Since however the decomposition of the cellulose generally runs more quickly than the splitting off of the methoxyl from the lignin we see an increase in the methoxyl content in decaying wood. This is clearly shown by the experiments of Bray and Andrews; but Fischer's and Schrader's studies of samples of peat from various depths of a deposit show that, with progressive humification, the increase first observed in the methoxyl content is followed by a decrease as shown in table 1.

As early as forty years ago Hoppe-Seyler made extensive studies of the decomposition of cellulose by bacteria. He was convinced that this process takes place in nature on a tremendous scale. He was not, however, able to establish a relation between the fermentation of cellulose and the process of formation of humin substances, peat, and brown coals. He knew that plants contain substances which are extremely resistant to bacterial influences but he was unable to satisfy himself as to their nature. Today we know that this substance is lignin. Omelianski too carried out very painstaking and thorough studies on cellulose fermentation. He obtained, in addition to gaseous decomposition products such as hydrogen or methane, considerable quantities of acetic acid and butyric acid. Fischer and Schrader were

TABLE I
Content of methoxyl of peat from different depths (Fischer and Schrader)

	DEPTH	ASH	METHOXYL
	<i>m.</i>	<i>per cent</i>	<i>per cent</i>
Peat (Velen) 1	0	1 8	0 49
Peat (Velen) 2	0 9	1 7	1 22
Peat (Velen) 3	1 8	1 8	1 67
Peat (Lauchhammer) 3	Increasing depth	7 1	2 97
Peat (Lauchhammer) 4		6 8	2 73
Peat (Lauchhammer) 5		6 6	1 66

able to determine, by means of experiments with bacteria from garden soil, that fungus cultures established themselves only upon cellulose, lignin remaining free from them. Recently Wehmer tried to cultivate bacteria which would have the ability to attack lignin. These experiments were undertaken because of data from other sources indicating the existence of such lignin consumers. These experiments by Wehmer were fruitless, however, surely a proof that if there are lignin consumers they are extremely hard to cultivate whereas the cellulose bacteria can be obtained easily from any garden soil.

I have already mentioned that pressure-oxidation furnished the proof of the aromatic structure of hard coals. Fischer and Schrader therefore subjected all compounds which have any

relation to the formation of coal, that is to say sugar, cellulose, lignin, humic acids, and lignites, to pressure-oxidation and were thus enabled to arrange the substances named into two groups, those which yield furan derivatives, like cellulose and sugar, and those which give benzol derivatives, namely lignin, natural humic acids, brown coals, bituminous and anthracite coals. The results of pressure-oxidation are the best proof of the derivation of humus coal from lignin. Cellulose can still be detected in the lignitic brown coals in which the wood structure is completely retained. The lignites are not looked upon by Fischer and Schrader as normal brown coals but as a wood petrified in consequence of special conditions. The question may be raised whether the Fusain present in many hard coals may not be traceable to such cellulose residues.

If the formation of the humic acids is essentially conditioned by biological processes it must be assumed that physical factors played a part in the conversion of the humic acids and their anhydrides which form the humus of the brown coals into the humus substance of the hard coals.

The formation of hard coals (bituminous and anthracite) cannot be explained exclusively through the influence of the time factor; there must also have been some heat effect, due for example to the fact that the brown coals reached great geothermal depths because of their covering layers. Consequently coals in which such a heat effect did not occur because of a thinner layer above them have remained in the brown coal stage although from their geological strata they should really have been converted to hard coals. An example of this may be seen in certain Russian coals from the lower carbon layer.

To test this assumption Erdmann carried out the following experiments: He heated lignitic brown coals in an autoclave with half their weight of water for one hundred hours at 280 degrees, brown lignite containing 64 per cent carbon yielded a black coal with 91 per cent carbon; and the bitumen, which had been wax-like in the brown coal, went over into a viscous, fluorescent, paraffin-containing oil exhibiting the characteristics of hard-coal bitumen (table 2). As a result of this experiment Erdmann

came to the conclusion that a minimum temperature of about 300 degrees must have been necessary for the formation of hard coal. Under these conditions, the humic acids and humins of the brown coals were converted into the substances of hard coal.

Bitumen, the second essential constituent of humus coals, which, to be sure, only makes up a small percentage of the total

TABLE 2
150 grams lignite with 75 grams water during 100 hours heated to 280°

Before heating		PURE COAL	After heating		PURE COAL
	C H O (N) color	64 4 6 56 29 0 brown		C H O (N) color	91 3 5 7 3 0 black
	Benzene extract solid, brown, montan wax			Benzene extract viscous, fluorescing with paraf- fin wax 0.48%	
3 6%			0 48%		

TABLE 3
Extraction of coal by benzene

KIND OF COAL	Without pressure	Under pressure
	<i>per cent</i>	<i>per cent</i>
Saxon high bituminous brown coal	15 0	23 0
Rhenish brown coal	3 3	7 1
Bohemian brown coal	2 3	7 1
American lignite (North Dakota)	1 3	
Bituminous coal	0 1	6 6
German Cannel coal	1 1	4 0

mass of the organic substance of coal can be separated from the humus substance by different solvents.

The bitumen hitherto studied was extracted from the various brown coals with boiling benzol. The substances called bitumen B, extracted with benzol at about 270 degrees in the autoclave, are similar to the bitumens obtained at atmospheric pressure, but have no more precise information about them. The bitumen

content of the brown coals varies widely as can be seen from the data in table 3.

Today we have very complete information as to the composition of brown coal bitumen. Broadly speaking we may say that it consists of wax and resin-like substances, present in the individual coals in very variable proportions. A good idea of the distribution of wax and resin-like substances in the bitumen of brown coals from different sources can be obtained from the data of Graefe, given in table 4.

The wax-like constituents of brown coal bitumen were studied as early as 1852 by Brückner who isolated an acid of the formula $C_{28}H_{56}O_2$ from a brown coal from the brown coal fields of middle Germany and called it geocerinic acid. The work of Brückner

TABLE 4
Resin content of bitumen of brown coal

ORIGIN OF BITUMEN	RESINS
	<i>per cent</i>
Pyropissite	6 6
Saxon brown coal	16 5
Bohemian brown coal	31.5
Silesian brown coal	67.9
Rhenish brown coal	17 6
American lignite (North Dakota)	74 0

was apparently forgotten at that time for it was only through the investigation, carried out by Hell in 1901 of the so-called refined montan wax of Von Boyen that attention was drawn to this acid.

It was sometimes given the formula C_{28} and sometimes C_{30} by various workers and consequently I made a painstaking study of it with Kreutzer as a result of which I was able to show that the acid constituents of the bitumen of brown coal consist, not of a single acid but of an acid mixture which can be separated by fractional distillation of the methyl ester followed by fractional precipitation of the free acids with magnesium acetate. We were able to establish the presence of the acids C_{25} , C_{27} , and C_{29} , in the bitumens of the brown coals of central Germany and the presence of acids of still higher molecular weights appeared probable.

Of the two acids, C_{27} and C_{29} , we named the first carbocerinic acid and for the second we retained the designation montan acid. These two made up the greater part of the fatty acids of the bitumen in the brown coal from central Germany. A later study with Dilthey of the bitumen in Rhenish brown coal confirmed these findings and showed that the same acids occurred in the bitumen of other brown coals as in those of middle Germany.

The acids of the bitumen of brown coal can be looked upon as normal fatty acids for their melting points indicate that they connect smoothly with the already known normal fatty acids having an odd number of carbon atoms.

The alcohols esterified with the acids in the bitumen of brown coals from middle Germany were distinguished by Pschorr and Pfaff as tetrakosanol $C_{24}H_{50}O$; cerylalcohol $C_{26}H_{54}O$ and myricylalcohol $C_{30}H_{60}O$. In the bitumen of Rhenish brown coals Dilthey and I discovered, in addition to myricylalcohol, another unknown alcohol $C_{32}H_{64}O$ which we called bituminol. From the acid and saponification numbers, as well as from the quantitative preparative working up of brown coal bitumen, it appears that, in montan wax, we have to do with a mixture which contains about 25 per cent free fatty acid and 75 per cent real wax consisting of the esters of the fatty acids mentioned with aliphatic alcohols.

Our knowledge of the resin-like portion of brown coal bitumen is less extensive. It is only recently that Steinbrecher studied the resin-like constituent of the bitumen of brown coal from central Germany and came to the conclusion that we have to do with resinolic acid resins which are comparable with amber and therefore consist of free resinic acid, and resinic acids, esterified with resin alcohols. The strongly acid portions are very much like colophonic and colophenic acids, that is to say typical resinic acids. Between the composition of resin from montan wax and real earth resin there are of course quantitative, but no qualitative, differences.

The bitumen of hard coal, as it is extracted for example by benzol under pressure or by pyridine, can be split up by petroleum ether into a soluble oily portion and an insoluble solid portion. The oil bitumen consists of hydrocarbons while the solid bitumen contains oxygen-containing substances.

As early as 1913 Pictet extracted hydrocarbons from hard coal with boiling benzol and studied them. Later Hofmann

TABLE 5
Extraction of Saar bituminous coal by benzene (Pictet)
Benzene extract, per cent from the coal

UNSATURATED HYDROCARBONS	SATURATED HYDROCARBONS
Dihydrotoluene: C_7H_{10}	C_9H_{16}
Dihydro-m-Xylene: C_8H_{12}	C_9H_{16}
Dihydromesitylene: C_9H_{14}	$C_{10}H_{20}$
Dihydroprehnitene: $C_{10}H_8$	$C_{11}H_{22}$
$C_{11}H_{16}$	$C_{12}H_{24}$
$C_{14}H_{18}$	$C_{13}H_{26}$
Dihydrofluorene: $C_{13}H_{18}$	
$C_{13}H_{18}$	
$C_{17}H_{20}$	
Melene: $C_{30}H_{50}$; F.P. 62–63°	

TABLE 6
Extraction of Upper Silesian bituminous coal by pyridine (Hofmann and Damm)

PER CENT FROM THE COAL					
Total extract..					10-19
Neutral substances					1 6
Phenols					0 25
Paraffin wax					0 02
PARAFFIN HYDROCARBONS	OTHER SATURATED HYDROCARBONS				UNSATURATED HYDROCARBONS
$C_{21}H_{44}$	$C_{17}H_{30}$	$C_{17}H_{30}$	$C_{17}H_{30}$	$C_{22}H_{44}$	$C_{15}H_{20}$
$C_{22}H_{46}$	$C_{18}H_{34}$			$C_{23}H_{46}$	$C_{16}H_{20}$
$C_{23}H_{48}$	$C_{14}H_{26}$				$C_{17}H_{22}$
$C_{24}H_{50}$	$C_{15}H_{28}$				$C_{18}H_{22}$
$C_{25}H_{52}$	$C_{16}H_{30}$				$C_{19}H_{24}$
$C_{26}H_{54}$					$C_{21}H_{26}$
$C_{27}H_{56}$					
Methylanthracene $C_{18}H_{12}$					

and Damm subjected a large amount of hard coal from Upper Silesia to pyridine extraction, split up the products, and identi-

fied the hydrocarbons which they contained. Tables 5 and 6 give a summary of the most important results of the studies of Pictet and Hofmann and Damm. The hydrocarbons found in the two cases were not identical to be sure but broadly speaking they could be placed in the same class. One interesting hydrocarbon should be mentioned particularly, the saturated melene found in the coal by Pictet to which the formula $C_{30}H_{60}$ was assigned. According to the studies by Pictet and also by Fuchs this hydrocarbon can also be obtained from lignin.

Fischer, Broche and Strauch have shown that the oil bitumen causes the caking of the hard coal. There must however be a certain minimum quantity present to cause a sufficient softening and melting of the coal during the coking to produce a caked coke. The tendency to coking on the part of the coal is thus traceable to the solid bitumen while the force of the tendency is determined by the point at which the solid bitumen decomposes. The higher this point the greater the tendency.

In general the formation of the bitumen of coal is assumed to be traceable to a wax and resin content in the coal-forming plants. It is noteworthy that in his recent studies of beeswax Gascard has encountered the same acids as are found in brown coal bitumen. Cerotinic acid and melissinic acid to which Gascard gave the formulas C_{25} and C_{31} had already been known to be constituents of beeswax but this was not the case with carbocerinic acid, C_{27} and montan acid C_{29} . Though it would be premature to draw any conclusions from this discovery nevertheless it is noteworthy that the typical acids of brown bitumen, namely carbocerinic acid and montan acid occur, in a recently formed substance concerning the formation of which we have definite knowledge.

The beeswax acids with odd numbers of carbon atoms are the typical constituents of other waxes also but not of the animal and vegetable fats in which the glycerides of the much lower fatty acids with an even number of carbons predominate. It is worthy of remark that the latter acids are not found in fossil material, and this permits us to draw some conclusions as to differences in the stability of acids with odd and even numbers

of carbon atoms. This is indicated also by the findings of Fischer and Schneider who obtained only odd-numbered fatty acids from the pressure-oxidation of paraffin. In cracking individual hydrocarbons Skraup found similar differences in the stability of compounds with odd and even numbers of carbon atoms.

The conversion of the wax of the brown coal bitumen into the hydrocarbons of bituminous coal bitumen can be explained by a kind of pressure distillation as has been shown by the experiments of Erdmann.

Briefly we may now consider ourselves relatively familiar with the smaller part of coal bitumen. Of the chemical constitution of the real body of the coal on the contrary our knowledge is very sketchy although great progress has assuredly been made within recent years. It is doubtful whether a perfectly satisfactory explanation of the constitution is possible with the methods of classical organic chemistry. With these complicated mixtures of insoluble organic substances it will be necessary to follow the suggestions of Fischer in other fields of work that is to say we shall have to treat not single individuals but groups of related bodies by new methods and possibly success will be achieved, as in albumin and tanning chemistry, by the synthesis of similar substances.

Up to this point my remarks have only dealt with chemical alterations of the coal in so far as these reactions came into play in the problem of structure. The present endeavor of chemistry is to make a chemical raw material of coal which has hitherto been used almost exclusively as fuel.

Essentially we can arrange the chemical changes to which coal can be subjected into three groups;

1. Alteration through the action of heat alone.
2. The breaking up of the larger coal molecules into smaller chemically valuable ones by the action of oxidizing agents.
3. The splitting up of the large, non-melting infusible and insoluble coal molecule by the action of reducing and hydrogenizing agents, to soluble and oily substances—a process which is called popularly the liquefaction of coal.

The heating of coal in the absence of air for obtaining metallurgical coke or illuminating gas has, to be sure, been used for many decades, but the processes which occur thereby, particularly the reactions by which the aromatic anthracite coal tar results have only been explained very recently. If heated gradually from the temperature required for dryness to 325 degrees brown coals give off abundant quantities of gas which consist mainly of carbon dioxide and hydrogen sulfide. Bituminous coal on the contrary evolves no gas up to this temperature. Use is made of this behavior of brown coal in so-called Bertination, a kind of artificial carbonization which leads to a diminution in the oxygen content consequently to an increase in the heating value of the fuel.

On heating coal further from 350 degrees to 500 degrees decomposition sets in, crude tar and fixed gas being given off. In 1906 Börnstein first proved that crude tar is essentially different from the tar obtained at high temperatures in the coke ovens and in illuminating gas retorts. More intensive investigations of the coking of crude tars have been carried out by Franz Fischer and his co-workers. Crude tar consists essentially of hydrocarbons and phenols. The lowest boiling portions have the character of Caucasian gasoline. Benzol, naphthalene and carbolic acid, the typical constituents of the tar from cokeries, are not present or only in quite small quantities in crude tar which has not been superheated. We must assume that the crude tar hydrocarbons form from the bitumen of coal while the phenols are produced from the actual body of the coal. Schneider and Erdmann, who divided brown coal into bitumen, humic acids and residual coal insoluble in alkali, showed that the bitumen yields a large quantity of a tar poor in phenol, but rich in paraffin, while the humic acids yield only a small quantity of tar rich in paraffin with almost no solid paraffin wax. If we take into consideration the fact that the humic acids have an aromatic structure, the considerable formation of phenols, that is to say of benzol derivatives, is easy to understand.

In table 7 are given the average yields of primary tars obtained for various kinds of coal with their contents of phenols and solid paraffin wax.

Of the brown coals the "Schwel" coal from middle Germany, which is rich in bitumen, yields large quantities of primary tar containing much paraffin and little phenol, whereas we obtain a small quantity of tar rich in phenols from the Rhenish brown coals which are poor in bitumen. Of the brown coals, lignite furnishes the tar richest in phenols.

Of the hard coals the geologically or genetically youngest give the highest yields of primary tar. Since these coals are also richer in oxygen than those which are geologically older, the primary tar contains a large quantity of phenol which runs

TABLE 7
Tar, phenols and paraffin obtainable from various coals

KIND OF COAL	YIELD OF CRUDE TAR	CONTENT OF SOLID PARAFFIN IN THE CRUDE TAR	CONTENT OF PHENOLS IN THE CRUDE TAR
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
Schwel coal (Central Germany)*	24	29	15
Rhenish brown coal.....	7 6	13	37
Westerwald lignite.....	2.7		57
American brown coal (N. D.)	5 6		45
Gas flame coal.....	10-14	1-2	40-45
Gas coal.....	5-8	1-2	25-35
Fat coal	3-4	1-2	15-25
Lean coal	1 5		0
Cannel coal	29		5-10

* A kind of lignite rich in volatile matter.

parallel with the oxygen content of the coals and in the case of the gas flame coals makes up half of the primary tar. From the older coals, we obtain less and less primary tar with a diminishing content of phenol. The lean coals yield almost no primary tar.

The cannel coals yield a great deal of primary tar with a low phenol content, although they contain almost no substances soluble in benzol. We see here an essential difference between the sapropel and humus coals.

The residue from the distillation for primary tars, the semicoke, still contains about 15 per cent of volatile constituents which, on further heating to 1000 degrees, are largely given off in the form

of hydrogen accompanied by small quantities of methane hydrocarbons.

The gas evolved in the distillation of primary tars contains a large amount of hydrocarbons but only a little hydrogen. It has a heating value of about 900 B. t. u. per cubic foot which is much greater than that of coke oven gas.

The study of the distillation of primary tars and its products has finally cleared up the question as to the formation of aromatic hard coal tar. After Berthelot succeeded in converting acetylene into benzol the view was held for a long time that acetylene played an important rôle in the formation of the tar of coke ovens. The behavior of primary tar and its constituents, on heating to a high temperature, showed plainly however that the aromatic hard coal tar represents the thermal decomposition product of primary tar. The primary tar phenols are most important in the formation of coke-oven tar. As Fischer and Schrader have shown, they are reduced at 800 degrees with a good yield of aromatic hydrocarbons. At the same time, there occurs a splitting off of alkyl groups so that for example not only toluol, but benzol also forms from cresols. The behavior of the primary tar hydrocarbons in the coke oven differs with their constitutions. The aliphatic hydrocarbons split into smaller fractions and go off as gases like methane and hydrogen with deposition of soot. The naphthene hydrocarbons, which have a ring structure, suffer the same fate as the aliphatic to some extent, but in so far as they contain six-membered rings they are converted into aromatic hydrocarbons by the splitting off of hydrogen. The knowledge of this relationship explains also a fact which has long been known experimentally, that is to say that the yield of coke-oven tar increases with the oxygen content of the hard coal. As we have seen, these coals also give the highest yields of primary tar phenols which we must consider to contain the most important elements in the formation of the aromatic tars.

The serious attempts which have been made in Europe, particularly in Germany and England, in the field of low temperature distillation of hard coal are well known. The numberless types of furnaces which have been proposed are built essentially on

the two following principles. The coal, which is introduced into either horizontal or vertical stationary or rotating furnaces, receives the heat from the outside, through the wall of the furnace, or by direct transfer from hot gases serving as heat carriers. This method of operating can also be used successfully in furnaces which are built on principles similar to those of the externally heated furnaces.

Until the present time none of the numerous processes for lignites rich in volatile material have yielded entirely satisfactory economic results with hard coal although there can be no doubt, in view of the importance of the problem and the intensity with which it has been worked on, that a positive success is yet to be expected. With hard coal it is important for the economic success of the distillation that the semi-coke, the principal product of the process, be obtained in dense lumps suitable for transporting and storing. A distillation of hard coal for the sake of the oil alone has little prospect of being economically successful.

The purely thermal decomposition of coal at low or high temperatures does, to be sure, yield a series of chemically valuable liquid substances, but their quantities are generally small in comparison with the amount of coal used and in this connection, we speak with justice of by-products. In their production we are limited first of all by the possibility of marketing the principal product, in this case coke. For economic reasons, therefore, the quantities of the by-products which are valuable in and for themselves can not be increased at will.

In order to make a chemical raw material of coal, it must never be subjected to such chemical effects as convert the principal body of the organic substance of the coal into chemically valuable products. In the discussion of its chemical constitution, the oxidative break-down of the coal by pressure-oxidation, has already been mentioned, leading to aromatic carboxylic acids. It is not possible to predict today the future significance of this gentle combustion of coal. We have here, at any rate, a way of obtaining chemically valuable substances from coal.

Another possibility of getting from the complicated coal molecule to simple soluble and liquid substances consists in allowing

hydrogen, or reagents which give off hydrogen to act upon coal. This splitting up of the coal molecule was first achieved by Berthelot in 1869 by means of his classic hydriodic acid method. In addition to hard coal he hydrogenized artificial humic acids, charcoals, etc. and he says that in every case he obtained saturated hydrocarbons, particularly hexane and hydrocarbons with a number of carbon atoms divisible by six. Ten years ago we repeated the experiments but could obtain no such degree of liquefaction under the conditions cited by Berthelot. It was only when we used higher temperatures that we were able to confirm the Berthelot experiments. Nevertheless we made the interesting observation that the younger they are the more easily

TABLE C
Comparative hydrogenation of different coals with hydriodic acid

KIND OF COAL	COKE YIELD	SOLUBLE IN CHLOROFORM	
		Before hydro- genation	After hydro- genation
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
Gas flame coal.....	64	1.5	70
Fat coal.....	78	0.7	55
Semi-bituminous coal.....	85	0.6	18
Anthracite.....	89	0.5	12

hard coals are hydrogenized by hydriodic acid. The chloroform-soluble constituents formed by the hydrogenation were taken as the measure of this (table C).

The first experiments in the hydrogenation of coal by a method which could be transferred to large-scale operation were carried out in 1913 by Bergius and Billwiller who allowed molecular hydrogen to act upon finely pulverized coal at temperatures of about 450 degrees and pressures of several hundred atmospheres. Even in their first patent they state that they can convert 85 per cent of the coal to liquid, soluble, or gaseous compounds. Bergius expressly stated his process to be non-catalytic and as proof of it stated that he had also observed the formation of liquid products in an apparatus with a glass lining, that is to say under

exclusion of any possible catalytic effect of the iron autoclave wall. On the other hand it may be said with respect to this experiment that Bergius surely did not use an ash-free coal and that consequently the ash might have affected the reaction catalytically. As a matter of fact, in his process Bergius added iron oxide equal to about 5 per cent of the weight of the coal as he says to fix the sulfur which otherwise would favor the polymerization of the heavy oils. There are numerous publications by Bergius himself, as well as by other investigators, concerning the treatment of coal with hydrogen under pressure. The various experiments may be summarized as follows. In this case also the younger, and, to be sure, non-coking, coals are most suitable. They are most easily hydrogenized and give the highest yields of oil. In the Bergius process the consumption of hydrogen

TABLE 8
Hydrogenation of semi-coke from brown coal under pressure

Semi-coke	14% water	65-280° 63% Above 280° 20% Residue 17%	22% phenols 3% bases 75% neutral oils 87%	B.P. 180-215° 60% B.P. 180-260° 80%
	40% oil			

amounts to about 5 per cent of the weight of the coal or 625 cu. m. per ton of coal. In spite of this the total liquid reaction products contain no more hydrogen by weight than was originally present in the coal, for the hydrogen entering into reaction is later found again in the form of gaseous reaction products, methane and lower homologues which make up from 25 to 30 per cent of the coal. In order to obtain a clear picture of how the coal substance, which has been freed from tar, behaves on hydrogenation and, in particular, to get an idea of the composition of the oils formed, Fischer and Frey subjected brown coal semi-coke, obtained by careful distillation of Rhenish brown coal, to pressure hydrogenation. Forty per cent of oil which could be distilled was obtained from the semi-coke by this means. A study of this oil, undertaken by Ter-Nedden and myself, yielded the values shown in table 8.

We see that over 20 per cent of phenols are contained in the main body of the oil. They consist half of carboic acid and cresols, that is to say o- and m-cresol were found but no p-cresol was found. Noteworthy is the high content of basic constituents in the oil. They were very high-boiling and had an odor of the higher pyridine bases and quinoline. There were no lower boiling bases. The hydrocarbons obtained in the hydrogenation of brown

TABLE 9
Hydrogenation of semi-coke from brown coal
Boiling limits, ratio of C:H and density of different fractions

FRACTION	BOILING LIMITS	C:H	DENSITY
	°C.		
1	60-85	1:1 9	0 739
3	95-115	1:1 7	
6	135-145	1:1 5	0 850
12	100-115	1:1 2	0 933
	b. 35 m/m		
16	155-168	1:1 2	0 972

TABLE 10
Reduction of cresols with hydrogen under pressure

KIND OF SUBSTANCE USED	TEMPERATURE	TIME	HIGHEST H ₂ PRESSURE	STILL SOLUBLE IN ALKALI	FORMED HYDROCARBONS AND GASIFIED SUBSTANCE
	°C.	hours	atm.	per cent	per cent
m-Cresol	460	1½	245	92 6	7 4
p-Cresol.	460	1½	240	93 7	6 3
o-Cresol	460	7	240	86 8	13 2

coal semi-coke gave off an odor of gasoline or petroleum. Table 9 gives the atomic proportions of C:H and the boiling limits and densities of single fractions.

Since only small quantities of unsaturated hydrocarbons could be detected there must be some of cyclic nature and the densities obtained are in agreement with this. The occurrence of the phenols is to be explained by their great stability under the conditions of pressure hydrogenation. Experiments with pure

cresols showed that, at 460 degrees and 240 atmospheres hydrogen-pressure, for an experimental period of one to seven hours, not even 10 per cent can be reduced to hydrocarbons or converted into gaseous products (table 10).

Now since, according to Bergius, the coal should have passed through the hydrogenation apparatus in ten minutes no essential alteration of the phenols would take place once they had formed from the coal.

The hydrogenation of solid fuels can also be carried out with substances which give off hydrogen, for Fischer and Schrader

TABLE D
Hydrogenation of coal with sodium formate

ETHER-SOLUBLE PRODUCTS OF HYDROGENATION IN PER CENT OF COAL USED	
Bituminous coal	Brown coal
Anthracite..... 1.6	
Fat coal..... 9.2	
Semi-coke..... 9.8	
Lean coal..... 10.7	
Fat coal (liable to spontignation)..... 26.3	Lignite 26.8
	Semi-coke... .. 32.4
	Brown coal (soluble in alkali) .. 36.3
	Ulmic acids..... 37.1
Gas flame coal.. 39.2	Saxon "Schwel" coal..... 43.4
	Rhenish brown coal..... 45.0

have carried out this process with sodium formate. They made a determination of the ether-soluble constituents in the product of hydrogenation and obtained the figures shown in table D.

The youngest coals give the highest yields. A mixture of carbon monoxide and steam acts like sodium formate. Comparative experiments by Fischer and Schrader show that this mixture hydrogenizes even better than pure hydrogen, a fact which is probably explained by the fact that in this case we have the hydrogen in the nascent state (table 11).

The hydrogenation of coal consists not only in a reduction of

oxygen-containing compounds and an attachment of hydrogen to unsaturated substances but we must imagine that a loosening of the tight bonds of the molecule occurs and that in the moment of dissociation hydrogen then attaches itself to these fractions. Kling and Florentin have found that these temperatures of decomposition are at different points for different substances and they were able to prove that they generally correspond to the temperatures at which the individual substances can be hydrogenized.

The Bergius process has already been tried for many years, in a large experimental plant in Rheinau near Mannheim, but has not yet found practical application. The Gesellschaft für

TABLE 11
Hydrogenation of rhenish brown coal with CO + H₂O (Fischer and Schrader)
(Comparison with efficiency of H₂)

MEDIUM OF HYDROGENATION	PRESSURE	ETHER-SOLUBLE PRODUCTS OBTAINED (PER CENT OF COAL)
	<i>atm.</i>	
H ₂	90	5
CO (dry)	90	12
CO + H ₂ O	90	36

Teerverwertung of Duisburg-Meiderich has recently erected a plant for the Bergius process.

For many years the Badische Anilin- and Sodafabrik, now a part of the I.-G. Farbenindustrie has been occupied with the problem of the hydrogenation of coal and of course they wish particularly to use crude brown coal for obtaining oil. Their method has been briefly described in a lecture by Director Krauch of this company. According to him the process is very similar to that of Bergius in so far as hydrogen is made to act upon coal at those temperatures at which it breaks up into certain fractions. By varying the hydrogen pressure, the velocity of flow, and particularly by the use of certain catalysts, it is said to be possible to obtain the predominance of certain reaction products, particularly low-boiling hydrocarbons, in distinction from the Bergius

process in which no, or at least no specific, catalysts are used and only certain products can be obtained for each coal. Now it is possible, by the choice of certain catalysts, to direct the reaction along definite paths so as to get aliphatic or aromatic hydrocarbons or mixtures of both and thus obtain anti-knock motor fuel directly.

The most essential factor in the economical hydrogenation of coal is the obtaining of cheap hydrogen. Now the I.-G. Farbenindustrie has constructed a producer in which finely granular fuel, like coal dust, semi-coke, hard coal of poorer quality, containing a relatively large amount of ash, can be kept in suspension by an ascending current of air or steam. The sensible heat of the gas on leaving is used for preheating the fuel of the charge. I am told that an extraordinarily high performance is achieved with this producer. It is possible to pass 750 tons of crude brown coal through a producer having a cross-section of 12 sq. m. in twenty-four hours, and it is said that the thermal efficiency of the producer is unusually favorable. The cost of the water gas is lowered as a result of the fact that the producer can be charged with the cheaper crude brown coal.

The direct conversion of the organic substance of coal, consisting of complicated compounds, into simple carbon compounds is the one way of utilizing coal chemically. It can however serve as chemical raw material in another way, that is to say if we start from the coke or practically elementary carbon remaining after the thermal decomposition. A great deal of it is used as a reducing agent in the blast furnace and in the Haber-Bosch ammonia synthesis. It has already found application as a chemical raw material in the manufacture of calcium carbide and the related lime-nitrogen, acetic acid manufacture etc.

There are unsuspected possibilities in the chemical conversion of the water gas obtainable from coke. Work done within the last few years has shown that the most various organic compounds can be manufactured in this way, including methanol, synthol, hydrocarbons etc., but a detailed description of these problems must await another lecture.

It should be stated too that we are not restricted to any definite

coal for these syntheses but that it is also possible to employ other carbonaceous substances as raw materials, providing water gas can be obtained from them. Thus for example, it is possible to use poorer grades of fuel, anthracitic coal, and even crude petroleum and natural gas. These remarks will show that there are well-founded prospects for making coal the basic material of chemical industry. In particular the obtaining of liquid motor fuels, whether directly, by the high pressure hydrogenation of coal, or through water gas by catalysis, will surely play a very important part in those lands which have no deposits of oil. The question will now be raised as to what quantities of coal will be required for the building of such an industry based upon coal. The coal mine owners, who do not themselves work up the coal, are of course interested in the greatest possible demand and good sales. But a quite incidental calculation indicates that the quantities of coal which are used for the processes described are relatively small in comparison with the quantities which are used at present for fuels and in the iron industry. The coal miner therefore, in so far as he does not work up the coal himself, will not be too optimistic about the process. If however we consider the case from a general economic standpoint and from the standpoint of the most economical utilization of the mineral deposits of a country, a chemical utilization of the coal is only to be welcomed for it heightens its intrinsic value and so has a direct relation to the enrichment of the common wealth of the nation.

THE OXIDATION OF THE GASEOUS PARAFFIN HYDROCARBONS

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1. INTRODUCTION

The gaseous paraffin hydrocarbons are a veritable treasure house as a source of material for transformation into derivatives

of great utility. The quantity of gaseous paraffin hydrocarbons which is produced is of astronomical magnitude. They are avail-

TABLE 1
*Available supplies of commercial fuel gases and their content of gaseous paraffin hydrocarbons**

GAS	VOLUME	METHANE	ETHANE	PROPANE	BUTANE
		per cent	per cent	per cent	per cent
	<i>cubic feet</i>				
Natural gas†	1,750,000,000,000	85	9	3	1
Coke oven gas‡.	639,644,000,000	28	12	1	
Gas from refining of crude oil§	240,000,000,000	61	21	12	4
Coal and water gas¶.	210,743,000,000	13	3	0.3	
Cracked gas from pressure distillation of heavy oils**	200,000,000,000	55	18	5	2
Carburetted water gas¶.	112,186,000,000	13	3	0.3	
Oil gas¶.	24,289,000,000	40	15		
Coal gas¶.	7,411,000,000	31	1.0		
Propane and butane in natural gasoline calculated to gas volume††.	15,995,750,000				
Propane and butane in unblended refinery gasoline, straight run and cracked calculated to gas volume ††, §§	15,865,500,000				

* The gas analyses were approximated by G. A. Burrell from results of his observations.

† Hopkins, United States Bureau of Mines.

‡ Mineral resources of the United States, 1925—Part II page 601; Separate II: 30, "Coke and By-products in 1925."

§ Estimate from data furnished by G. A. Hopkins, United States Bureau of Mines.

¶ Department of Commerce, Statistical Abstract of the United States, 1926.

** Estimated by Egloff.

†† Estimated by G. A. Burrell.

‡‡ In a private communication to the authors, G. G. Brown estimated the average propane content of unblended refinery gasoline, straight run and cracked, as about 0.5 per cent by weight and the average butane content about 3.0 per cent.

§§ The production of unblended refinery gasoline, straight run and cracked, is estimated by the Bureau of Mines at 12,537,000,000 gallons. Oil Gas J., 26, No. 41, p. 120 (1928).

able in tremendous quantities in natural gas, and are also produced in quantity from crude oil, in the cracking of oils, in the

TABLE 2
Volumes of gaseous paraffin hydrocarbons available from commercial fuel gases (in cubic feet)

GAS	METHANE	ETHANE	PROPANE	BUTANE
Natural gas.	1,487,500,000,000	157,500,000,000	52,500,000,000	17,500,000,000
Coke oven gas.	179,100,320,000	76,757,280,000	6,396,440,000	
Gas from refining of crude oil.	146,400,000,000	50,400,000,000	28,800,000,000	9,600,000,000
Coal and water gas.	27,396,590,000	6,322,290,000	632,229,000	
Cracked gas from pressure distillation of heavy oils.	110,000,000,000	36,000,000,000	10,000,000,000	4,000,000,000
Carburetted water gas.	14,584,180,000	3,365,580,000	356,558,000	
Oil gas.	9,715,600,000	3,643,350,000		
Coal gas.	2,297,410,000	74,110,000		
Propane and butane in natural gasoline calculated to gas volumes.			1,941,750,000	14,051,000,000
Propane and butane in unblended refinery gasoline, straight run and cracked, calculated to gas volumes.			3,301,500,000	12,564,000,000
Summary				
Methane.				<i>cubic feet</i> 1,976,994,100,000
Ethane.				334,062,610,000
Propane.				103,928,477,000
Butane.				57,715,000,000
Total.				2,472,700,187,000

carbonization of coal, and from carburetted water gas. The volume of methane, ethane, propane and butane available in the United States during the year 1927 was over 2,472,000,000,000 cubic feet.

The present major use of the gaseous paraffin hydrocarbons is for combustion. There are higher uses to which at least a portion of the methane, ethane, propane, and butane present in commercial fuel gases may be put. They may be converted, for example, into useful products such as alcohols, aldehydes, acids and resins by means of oxidation with air, ozone, or chemical reagents.

The volume of the various industrial gases containing methane, ethane, propane, and butane which are available yearly, are shown in table 1.

The volumes of the gaseous paraffin hydrocarbons contained in these gases are shown in table 2.

By oxidation these hydrocarbon gases may be converted into methyl, ethyl, propyl and butyl alcohols, formaldehyde, acetaldehyde, propionaldehyde and butyraldehyde, the acids formic, acetic, propionic, and butyric and resins.

To give an idea of the enormous potentialities of hydrocarbon oxidation, the theoretical yields of methyl, ethyl, propyl and butyl alcohols obtainable from the available gaseous paraffin hydrocarbons have been calculated as follows:

ALCOHOLS	GALLONS
Methyl.....	21,519,328,930
Ethyl.....	5,817,493,000
Propyl.....	2,588,750,000
Butyl.....	1,754,600,000

To be sure, much study has already been devoted to hydrocarbon oxidation. The reactions are complex and lead to mixtures of products, frequently substances of little value such as oxides of carbon which are obtained in largest amount. But as one analyzes the work which has been done, the impression gained is not that of the completeness, but rather of the frag-

mentary state of our knowledge. One result of oxidation on a large scale is the production of a mixture of formaldehyde and methyl alcohol from natural gas as a by-product in carbon black manufacture. There is no doubt that many other oxidations can be made useful. The vastness of the field, and the rich rewards awaiting those who can direct these reactions, as yet largely uncontrolled, to the production of useful products, make it an enticing opportunity for research.

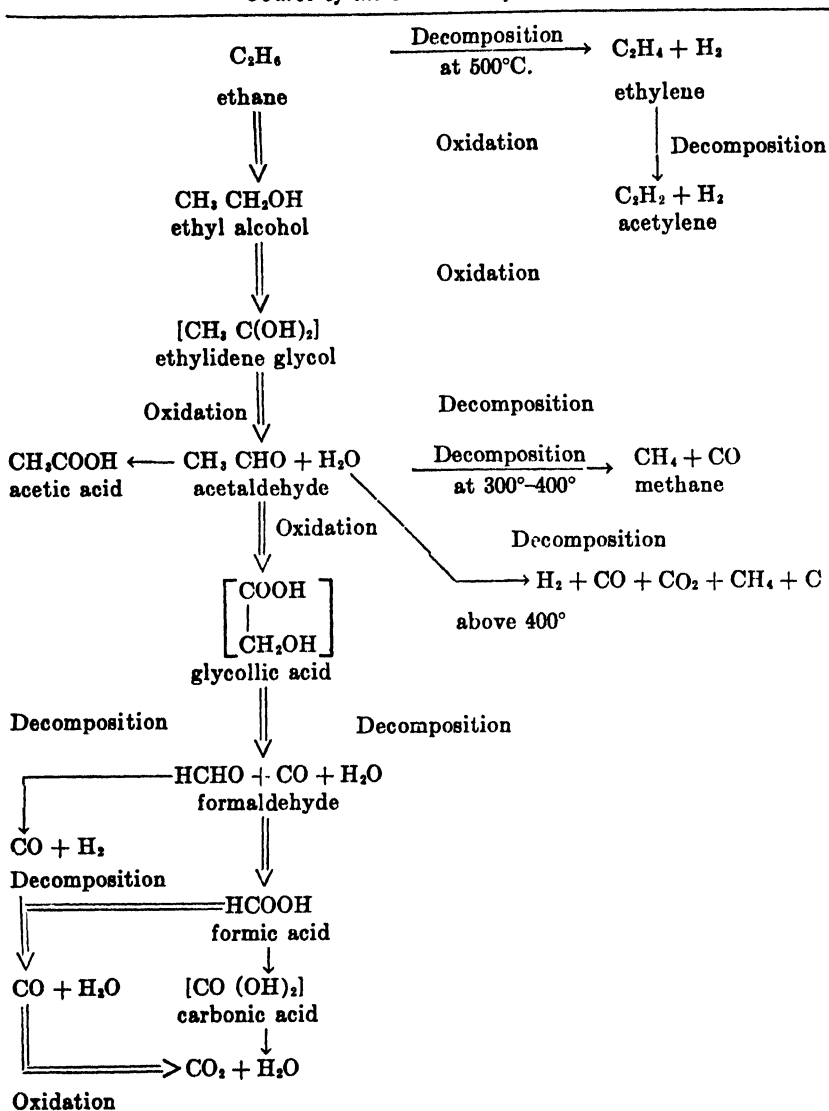
The oxidation of the gaseous hydrocarbons has attracted attention at least since the time of Volta (1), who supposed that the aurora borealis might be due to combustion of methane in the air under the influence of lightning. One almost regrets that Davy (2) conclusively disapproved this interesting hypothesis by showing that when diluted with more than seventeen parts of air, methane will not burn.

The studies carried on since early times have shown that although the gaseous paraffins do not react with oxygen in anything like the dilutions in which they occur in the atmosphere, they nevertheless undergo diverse oxidation reactions, giving rise to nearly every product theoretically possible. In the literature on their oxidation one finds, in addition to the ultimate products, water and carbon dioxide, the identification of hydrogen, carbon, carbon monoxide, alcohols, aldehydes, acetone, acids, saturated and unsaturated hydrocarbons, resins, (probably aldehyde polymers) and traces of hydrogen peroxide. The difficulty of controlling the reactions to give a single desired product is to be attributed to the greater ease of oxidation of many of the primary oxidation products than of the paraffins used as starting material.

The mechanism of hydrocarbon oxidation which has gained widest acceptance involves the stepwise formation of hydroxyl compounds, each of which may lose water and break down in one or several ways. This theory was put in definite form by Bone (3). As an example of its application the oxidation of ethane is represented graphically in table 3.

One of the most convincing lines of evidence for this oxidation mechanism, according to Bone and Drugman (5), is the formation of water and carbon in rapid hydrocarbon combustion. This is

TABLE 3
Course of the oxidation of ethane



The double lines above indicate the supposed course of the main reactions. Compounds not actually isolated are enclosed in brackets. Table 3 was prepared from the results obtained by Bone (3, 4) and his co-workers.

not consistent with the earlier mechanism proposed by Kersten (6) and revived by Misteli (7) which involved the preferential combustion of carbon. Bone and Drugman (5) write that two explanations seem possible to account for the appearance of water and carbon when a mixture of the composition $C_nH_{2n+2} + \frac{n}{2} O_2$ is exploded, "namely, (1) that, as at lower temperatures, an aldehyde and steam are formed at an early stage, for example:



the aldehyde would then probably decompose, yielding carbon monoxide and the lower paraffin, and a similar process would be repeated until at length acetaldehyde would break down into carbon, hydrogen, methane, and carbonic acid; or (2) that the primary oxidation product $C_nH_{2n+1}OH$ might decompose into $C_nH_{2n} + H_2O$, the olefin subsequently being burnt in its own peculiar way. In either case, the end result with a mixture $C_nH_{2n+2} + \frac{n}{2} O_2$ would be much the same."

A stumbling block in the way of the unquestioned acceptance of the hydroxylation theory is the failure of Bone, in spite of careful search, to isolate methyl alcohol as a product of the oxidation of methane by oxygen or air, although formaldehyde was found in sufficient amounts to allow its easy identification. Indeed, Wheeler and Blair (8), although favoring the theory of Bone, write "an excess of oxygen inhibits the oxidation of methane little, if any, more than an excess of methane, so that if the law of mass action applies, the equimolecular reaction to formaldehyde would seem to be occurring." In view, therefore, of the lack of absolute proof of Bone's oxidation mechanism, one may fairly ask whether some of the other oxidation theories do not fit many of the experimental facts equally well. The idea of oxidation by dehydrogenation so successfully applied by Wieland (9) to the oxidation of alcohols and to many other oxidation processes may here find application. Or dissociation, as postulated by Nef (10) may be involved. Callendar (11) has brought forward proof that knocking in the cylinder of an internal combustion engine is due

to the formation of organic peroxides. Such peroxide formation may be a step in other hydrocarbon oxidation processes.

Most of the investigations on gaseous paraffin oxidation have been carried out by the simple heating of the hydrocarbon mixed with oxygen or air. Considerable study has been made also of catalytic oxidation, of oxidation with chemical reagents, of ozone oxidation and of oxidation by such special means as the silent electric discharge, alpha radiation and bacteria.

Flame propagation with the related subjects of ignition temperatures and the limits of inflammability of gaseous mixtures are, strictly speaking, phases of hydrocarbon oxidation, but as these topics will be discussed fully in another paper on the physical and chemical constants of the paraffins, they are given here but this brief mention.

2. THE OXIDATION OF METHANE

a. General

Carbon monoxide, carbon dioxide and water have usually been the chief products obtained in the many experiments which have been made on the slow oxidation of methane. Bone and his co-workers proved, however, that formaldehyde is formed in the early stages of the oxidation, and in some of their experiments they also detected formic acid. Winter (12) obtained small amounts of free carbon when purified mine gas (methane 80 per cent, nitrogen 20 per cent) was exploded with air or oxygen. According to him, the free carbon did not arise from the incomplete combustion of methane, but from an equilibrium in which carbon dioxide and hydrogen participated. Hydrogen often appears in the reaction when an amount of oxygen insufficient for complete combustion is used. None of the earlier work showed methyl alcohol to be in the oxidation products of methane, but in 1922 Elworthy (13) stated that under the action of the silent electric discharge, mixtures of methane and oxygen gave a viscous liquid containing methyl alcohol, along with formaldehyde, polymerized aldehydes, resins, and formic acid. The formation of other aldehydes and of resins may be due to the polymerization of

formaldehyde, which under favorable conditions is produced in relatively large quantities. Aldehydes, formic acid and traces of alcohols have also been produced by the oxidation of methane with ozone.

This variety of oxidation products is readily accounted for by the hydroxylation theory of Bone. The course of the slow oxida-

TABLE 4
Course of the oxidation of methane

	CH_4	Methane
	\Downarrow	
	CH_3OH	Methyl alcohol
	\Downarrow	
	$[\text{CH}_2(\text{OH})_2]$	Methylene glycol
	\Downarrow	
	$\text{CH}_2\text{O} + \text{H}_2\text{O}$	Formaldehyde
	\Downarrow	
	H COOH	Formic acid
	\Downarrow	
	$[\text{CO}(\text{OH})_2]$	Carbonic acid
	\Downarrow	
	$\text{CO}_2 + \text{H}_2\text{O}$	Carbon dioxide and water
Decomposition	$\text{CO} + \text{H}_2$	
Decomposition	$\text{CO} + \text{H}_2\text{O}$	
Oxidation	$\text{CO}_2 + \text{H}_2\text{O}$	

Double lines show the usual course of the oxidation. Compounds that have not been isolated are enclosed in brackets.

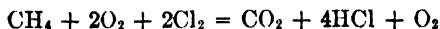
tion of methane according to Bone's theory is shown in table 4, which is the outline form constructed by Wheeler and Blair (14).

b. Oxidation by oxygen and air

The numerous investigations which have been made of the oxidation of methane will be taken up in approximately chronological order.

In 1861, as a part of work on the luminosity of gas flames, Kersten (6) made a careful study of the complete and incomplete combustion of methane. He concluded that while at times some free carbon forms, the carbon is normally oxidized to carbon monoxide before the hydrogen is reacted upon.

Schlegel (15) burned mixtures of methane with oxygen and chlorine, writing for the reaction the equation:

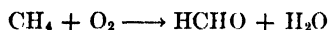


The combustion was preferential, the oxygen combining with the hydrogen only when there was a deficiency of chlorine, while no reaction of chlorine and carbon occurred. With insufficient oxygen for complete combustion, carbon monoxide was formed.

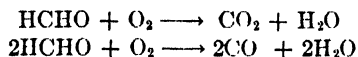
By continuously removing the products of the reaction from an apparatus devised to circulate methane and oxygen at 450°–500°, Bone and Wheeler (16) were able to show that neither hydrogen nor carbon was formed at any stage in the oxidation, and that although the final products of the reaction were normally carbon monoxide, carbon dioxide and water, there was a transient formation of formaldehyde. They were able to obtain this substance in amounts up to 22 per cent of the methane reacting, when it was removed from the sphere of action as rapidly as produced by passing the reaction mixture through cold water immediately on leaving the heating zone.

These workers concluded that the oxidation of methane involved the following steps:

1. The simultaneous formation of formaldehyde and water:

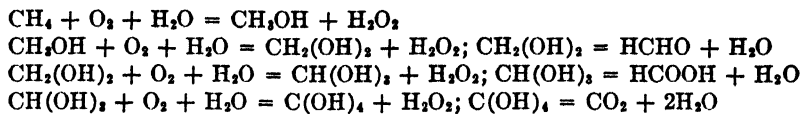


2. The further oxidation of the formaldehyde to carbon monoxide, carbon dioxide and water:



A later paper by Bone (17) dealt with the incomplete burning of methane to carbon monoxide and hydrogen.

Using this work as substantiation, Armstrong (18) claimed that the slow oxidation of methane was a series of hydroxylations in which water entered into the reaction and hydrogen peroxide was formed:



This would make carbon monoxide a secondary product, not resulting directly from the oxidation of methane. The validity of Armstrong's mechanism was brought into question, however, by the work of Bone and Andrew (19) on acetylene, which showed that water was not essential to hydrocarbon oxidations.

In the work of Wheeler and Blair (14), carefully purified methane mixed with oxygen was similarly passed through a circulating system in which it was repeatedly heated and the products of reaction promptly removed from the gas mixtures. They state: "A short time of heating and a slow oxidation are the principal factors in obtaining a good yield of formaldehyde. If the oxidation be vigorous it is formed in such a large proportion that it rapidly decomposes. A long time of heating has similar effects." The amount of formaldehyde isolated from the mixture after oxidation varied from 0.25 mgm. per liter of gas passed through the apparatus at 665° and a time of heating of 0.8 second to 2.9 mgm. at 740° with the same heating period or 720° when the gas was heated one second. Far larger amounts of formaldehyde than this were formed, but decomposed in the process to carbon monoxide and hydrogen. The time of heating had least effect on the yield of formaldehyde when methane was present in excess, as the lower the concentration of this product the greater its stability. At high temperature an excess of methane and the presence of steam both tended to increase the yield.

In experiments without circulation of the gas mixture a little formaldehyde was formed up to 820°, but above this temperature its presence could not be established, probably because of its rapid decomposition.

In a second paper Wheeler and Blair (20) reported studies, carried out by means of a circulation apparatus, following the action of oxygen on mixtures of methane and ethylene and their primary oxidation products. Coal gas, which contained these hydrocarbons in about the desired proportions and also considerable amounts of carbon monoxide and hydrogen, was diluted with about one-fifth of its volume of nitrogen to increase its explosive range, and as much oxygen added as was possible without rendering the mixture explosive. The mixture was then heated.

"As the temperature rises, first one and then another constituent commences to interact, and the rates of interaction rapidly increase until they appear to come into a constant ratio to one another. A comparison of these rates shows how it is that carbon monoxide and water are the chief products of the slow oxidation of methane under conditions in which formaldehyde decomposes, for at these temperatures and times of heating hydrogen is first attacked, next methane, and then carbon monoxide. The rapid increase at high temperatures in the rate of oxidation of carbon monoxide explains the presence of carbon dioxide in the products at such temperatures."

"The rates of oxidation of the hydrocarbons are not affected by the presence of intermediate products, although these dilute the reaction mixture. The yield of formaldehyde was slightly lower in these experiments than that obtained with methane, probably owing to the ethylene present giving a lower yield than methane. Decomposition of formaldehyde may also be induced by simultaneous oxidation of hydrogen, etc."

The yield of formaldehyde varied with the temperature and time of heating much as in the earlier experiments.

Bone and Drugman (3) showed that methane may be oxidized below its ignition point, and that water and formaldehyde are among the first reaction products.

Wieland (9) presented the hypothesis that the formic acid which could be detected in the methane flame was probably formed by the decomposition of the methane into carbon and hydrogen and the immediate reaction of the carbon with water to give carbon monoxide, which was then converted into the acid. When moist methane was passed through a hot tube, it yielded carbon dioxide and hydrogen.

Burgess and Wheeler (21) observed in the study of several mixtures of oxygen and methane that as the proportion of oxygen was increased, more and more of the hydrocarbon was completely burned. With one and one-half times as much oxygen as methane present, half of the methane burned to carbon dioxide and the balance to carbon monoxide, while with the oxygen present in less than this ratio the main reaction was represented by the equation:



These investigators held that there was a preferential burning of hydrogen rather than of carbon monoxide in all the mixtures in which the ratio of oxygen to methane was greater than 1.5. They also reported that the propagation of flame in limit mixtures formed carbon monoxide, hydrogen and steam in equal volumes.

Several patented processes cover the preparation of formaldehyde by the incomplete combustion of methane-air mixtures. In the method of Gruszkiewicz (22), a flame is formed by the partial combustion of the gas mixture beneath and partially within a perforated reaction tube closed at the top. The tube is preferably surrounded by a cooling vessel to reduce the temperature of the gaseous oxidation products immediately after their exit from the tube. The stream of hydrocarbon and air coming to the flame is heated to effect a rapid oxidation.

Lüttgen (23) also cooled the burner tube of a perforated Bunsen burner and interrupted the flame by devices to lower the temperature of the gases. A similar idea inspired the patent of Kunheim (24) in which the gases formed in a methane flame were quickly cooled by directing a jet of gaseous or liquid cooling medium against the flame. Behrens (25) claimed the preparation of formaldehyde by heating methane with a quantity of oxygen insufficient for complete combustion, the reaction being controlled by regulation of the amount of heat supplied. In Walter's (26) method, a mixture of methane, air and water vapor was subjected to high temperature for a short period. The same worker (27) proved in a simple fashion the production of formaldehyde when methane burns by allowing a small methane flame to impinge against snow or cold water, which was then tested for the aldehyde.

In a patent of the I. G.-Farbenindustrie Akt.-Ges. (28), methane, heated to 900° is passed into a flame zone in a quartz tube, where it meets a divided stream of oxygen. Besides unconverted methane, the resultant gaseous mixture contains water vapor, hydrogen, carbon monoxide and acetylene. As an alternative apparatus an iron tube lined with a refractory material and filled with lumps of a porous substance over part of its length may be employed. The yield of acetylene is increased if the products leaving the tube, whose temperature approximates 1000° are heated to 1200° in an electric furnace.

Berl and Fischer (29) investigated the oxidation of methane by air between 500° and 900° , passing various mixtures through heated tubes. A maximum of 1.8 per cent of the methane was converted to formaldehyde.

Tropsch and Roelen (30) passed mixtures of methane and air through quartz tubes heated in an oven. The formaldehyde produced was absorbed in water and determined by titration with standard iodine solution. They studied the effects of varying the methane-oxygen ratio in the gas, the diameter of the tube, the reaction temperature, and the velocity of the gas through the tube. The optimum concentration of methane for the formation of formaldehyde was 16 per cent, which at a temperature of 1000° gave 1.2 per cent of the theoretical yield. The best results were obtained with tubes 4.0 mm. in diameter and with a gas velocity of twenty meters per second, the gas being in the heated tubes about one one-thousandth of a second. The highest concentration of formaldehyde was obtained with equal volumes of methane and oxygen. With increase in the reaction temperatures, the absolute quantity of formaldehyde produced became greater, but the yield per unit of methane decomposed diminished. Based on the total methane entering the system the best yield of formaldehyde was 5.96 per cent at 1000° . Of the methane actually burned, 70 per cent could be converted into formaldehyde at 700° , but the formaldehyde concentration in the products was extremely low.

Brutzkus (31) invented a process for oxidizing methane to formic acid within the cylinder of a power driven compressor. The

hydrocarbon and oxygen, in combining proportions, were introduced into the compressor at such a rate that when the piston had completed two-thirds of its stroke the gases were under a pressure of thirty atmospheres and at a temperature of nearly 500°. During the remainder of the stroke, air, independently compressed to forty-five atmospheres, was introduced into the cylinder in a finely divided stream to produce a cooling effect and to increase the oxygen content. At the end of the compression stroke the gases were discharged and the formic acid was absorbed by water. The residual gases were then drawn back into the system to be retreated.

Bone, Davies, Gray, Henstock, and Dawson (32) exploded mixtures of methane and oxygen at constant volume under pressures of ten to fifty atmospheres. They formulated the reaction according to the mechanism of Bone and Drugman (3) as follows:



They also investigated methane-hydrogen, and methane-carbon monoxide mixtures, and showed that the "affinity" (really reaction velocity) of methane for oxygen in explosions was at least twenty to thirty times as great as that of hydrogen.

Winter (12) found that in the explosive combustion of methane-air mixtures containing 5.0 to 9.2 per cent methane the oxidation was essentially complete, while with from 9.2 to 14 per cent methane the products of combustion always contained carbon monoxide. The maximum of the explosion lay at 9.2 per cent methane rather than at the theoretical 9.5 per cent, a slight excess of oxygen being necessary for complete combustion.

Ledbury and Blair (33) have pointed out that for the preparation of formaldehyde from methane on a commercial scale, the use of oxygen rather than air is essential, since the presence of diluents hinders the reaction at temperatures which give good yields. In order to conserve oxygen, as well as methane, they recommend that the oxidation be carried out in a circulating system, gas being withdrawn periodically and fresh methane and oxygen admitted to ensure suitable concentrations of the reactants.

From the results of their laboratory experiments, these inves-

tigators have stated the conditions suitable for the production from methane of one ton of formalin per twenty-four hours. A mixture having the initial composition of approximately 80 per cent methane and 20 per cent oxygen would be circulated, passing through heating and absorbing zones. A temperature of 700° and time of heating of one second are suggested, which should give about 2 mgm. of formaldehyde per liter of gases leaving the reaction zone. It is estimated that 30 per cent of the methane consumed could be recovered as formaldehyde. A volume of methane amounting to 128,000 cubic feet, and 69,000 cubic feet of oxygen would be required per day. The cost of operation is estimated at \$180 per ton of formalin exclusive of the cost of methane. It is quite apparent that as far as their process is concerned their statement is true that: "The oxidation of methane on a technical scale for the manufacture of formalin can only be considered as an economic proposition if methane is obtainable in quantity at a low or even nominal cost." It is believed, however, that a far more efficient process than this can be devised, even with the present state of our knowledge of oxidation.

c. Catalytic oxidation

Much study has been given to the action of catalysts in promoting the reaction between oxygen and methane. A large proportion of the oxidation processes which have been proposed for commercial application are catalytic. The catalysts that have been employed cover a wide field, ranging from pumice, asbestos, and sand to the noble metals and even to the alpha radiation of radon. As a rule, the catalyzed oxidations are controlled more easily than those not catalyzed.

A recent editorial (34) appearing in *Industrial and Engineering Chemistry* states that thousands of gallons of methyl alcohol are being produced daily by the catalytic oxidation of natural gas. The details of this process are not disclosed.

A process of oxidizing natural gas is reported briefly in the *Refiner* (35) as follows:

"The process is one to catalytically produce methyl alcohol from natural gas, and at the same time conditions of heat and pressure are productive of oil falling in the gasoline range of boiling points. Conversion is effected at proper temperature conditions of pressure and temperature in both steam and natural gas in the presence of a catalytic agent. Field tests which led to the construction of the commercial unit resulted in the yield of 2.5 gallons of methyl alcohol and 2 gallons of oils per thousand cubic feet of gas passed through the system. High pressure equipment of special design is employed."

It was privately stated to the authors during the meeting of the American Chemical Society at St. Louis in April, 1928, that a mixture of methyl alcohol and formaldehyde was being recovered commercially from stack gases produced during the production of carbon black.

Coquillion (36) early found that in the presence of a red hot spiral of platinum or palladium, methane and air yielded formic acid. The palladium was the more powerful catalyst, although after a while it became brittle and lost weight. Because of its importance in the separation of hydrogen and methane in gas analysis, oxidation by palladium has been investigated repeatedly. Hempel (37) reported that methane and oxygen did not burn when passed over palladium at 100°, but that the reaction began at 200°. Winkler (38) stated that methane was not burned when passed over palladium asbestos in a tube heated to incipient redness before introduction of the gas stream while Brunck (39) reported that in this method the thread of catalyst might glow without causing oxidation of methane. On the other hand, Nesmjelow (40) claimed that palladium asbestos oxidized methane at as low a temperature as 150°. Phillips (41) found the lowest temperature for the combustion of methane in the presence of this catalyst to be between 405° and 451°. Denham (42) gave the beginning of oxidation as lying within the range 514° to 546° and proved that the catalytic action of the palladium was not due to superficial oxidation. After a very careful investigation, Richardt (43) concluded that by using palladium wire at 450°, little noticeable oxidation of methane took place, but at 700° there was rapid combustion. Probably the conflict between the results

of these different investigators is due to the fact that as a rule no clear distinction was made between the temperature of the vessel containing the catalytic mass and the temperature of the center of the catalyst. Besides this, sometimes palladium wire was used, at times palladium asbestos in a fine capillary tube and in other experiments palladium black in a tube of large diameter. These differences in the experimental methods would naturally lead to discordant results.

Campbell (44) found that methane mixed with air was not oxidized when passed over palladized copper oxide at temperatures below 455°.

A large share of the work on the catalytic oxidation of methane has had as its goal the preparation of formaldehyde. This is particularly true of the numerous processes covered by patents. These have been summarized by Roelen (45).

Glock (46) obtained formaldehyde from methane and air by passing equal volumes of the two gases over granulated copper. He also prepared this aldehyde by reaction of methane with oxygen in the presence of pumice, asbestos or a mixture of these with copper at about 600°. The several passages of the gas mixtures over the catalyst were interrupted by scrubbing and addition of air. No formaldehyde or methyl alcohol was produced when platinum was used as an oxidation catalyst, though this metal was satisfactorily used for removing hydrogen from the mixture by preferential combustion.

The Sauerstoff und Stickstoff-Industrie, Hausman and Company (47) patented a process for making formaldehyde and also methyl alcohol and formic acid by passing methane and air or oxygen over bark or fatty substances at 30 to 50°. However, this scarcely plausible procedure, when tested by Bantlin (48) yielded no trace of formaldehyde. Von Unruh (49) also employed tan bark and similar materials for oxidation of methane to methyl alcohol, formic acid, and formaldehyde, the last being claimed as the chief product.

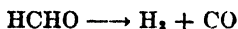
In 1912, in a publication on the Chemical Technology of Organic Compounds, Wöhler (50) stated that all the experiments on the commercial oxidation of methane to formaldehyde up to that

time had been unsuccessful in spite of the need for this product, and the enormous waste of natural gas then occurring. In tests which he described, the oxidation of methane by passing it over nickel or silver gauze at a temperature of 500 to 550° gave only 1 to 2 per cent of formaldehyde. Above this temperature the reaction was of no value. He attributed this failure to the fact that at the temperatures mentioned or above them, the decomposition of methyl alcohol, the primary product of the oxidation, was very rapid, while at lower temperatures its velocity of formation was too low for the process to be of any utility.

A patent of the Verein für chemische Industrie in Mainz (51) claims the formation of a small proportion of formaldehyde when a mixture of about three parts of methane and one hundred parts of moist air is conducted over a metallic surface of copper or silver, for example, at 150° to 200°.

Bone (52) observed that approximately eighty per cent combustion of the hydrogen occurred when a mixture of methane, oxygen, and hydrogen in the molecular proportions 1:1:2 was passed over chamotte at 500°. It is interesting to compare these results with those of Bone, Davies, Gray, Henstock and Dawson (32), on the explosion of methane, hydrogen and oxygen mixtures. In their work, the methane reacted with the oxygen at a very much higher rate than did the hydrogen.

Wheeler and Blair (14) extended their experiments on the direct oxidation of methane to include the use of catalysts. In the oxidation of this hydrocarbon in the presence of metals and their oxides, even with a very short time of heating, they could detect no formaldehyde. "This is not surprising. The formaldehyde produced in our circulation experiments is in a concentration much greater than that given by the equation:



The rapid cooling enables it to be isolated before equilibrium is attained or further oxidation can occur. But with catalysts the true equilibrium is attained almost instantly at the temperatures necessary to oxidize methane. The composition of the final gas, however, leads us to believe that catalysts do not change the course

of the oxidation of methane, and that with very high rates of gas passage some formaldehyde might be detected in the exit gases. . . . The action of surfaces was similar to that of catalysts, but much less pronounced. Formaldehyde was frequently detected when they were used."

These investigators (20) also studied the effect of catalysts on the oxidation of methane and ethylene mixed with their primary oxidation products. They found that using pumice, at low temperatures, the oxidation and decomposition of the intermediate products were accelerated more than the oxidation of the hydrocarbons themselves, while at high temperatures the rate of oxidation of the latter increased, so that hydrogen and carbon monoxide accumulated. Similar results were obtained using ferric oxide as catalyst. By using mercury the oxidation of ethylene, carbon monoxide and hydrogen was accelerated, but not that of methane.

A process patented by H. Otto Traun's Forschungs-Laboratorium (53) consisted in oxidizing methane or natural gas in the presence of ammonia in tubes of copper, silver, nickel-steel, iron or its alloys at a high temperature to give hexamethylene tetramine. In an example, six volumes of methane and twelve volumes of oxygen or a corresponding quantity of air were mixed with four volumes of ammonia and passed through a reaction space within a copper or silver tube, which had been pressed flat; for a distance of about 8 cm., from a normal diameter of 15 mm. to a separation of the walls of from 1 to 2 mm. throughout the constricted portion. When the reaction was carried out at reduced pressures, the flat portion of the tube was heated to 500° to 700°, but when the gases were allowed to interact at ordinary pressure it was found advisable not to have temperatures higher than 300° to 500°. The yield of hexamethylene tetramine was said to be approximately 70 per cent of the methane decomposed. Schönfelder (54) however, was unable to carry out this process successfully, and Wheeler and Blair (14) stated that while ammonia has some stabilizing effect on the formic acid produced in methane oxidation, it does not stabilize formaldehyde.

According to a patent of the Thermal Industrial and Chemical Research Company (55) the partial oxidation of methane may be

accomplished by passing a mixture of sixty to eighty volumes of methane and forty to twenty volumes of air (or its equivalent of oxygen) in the form of fine bubbles through molten metal heated to 350° to 400°. The unchanged gases and the vapors of formaldehyde which escape from the reaction vessel are then treated to collect the formaldehyde.

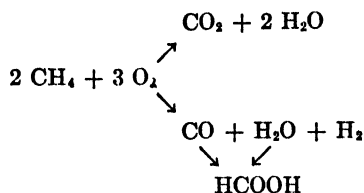
Elworthy (13) found that passing natural gas (containing eighty per cent methane) and oxygen over such catalysts as magnetite and other oxides of iron, oxides of copper, silver, thorium, cobalt, vanadium, and uranium, borosilicate glass, and platinum gave traces of formaldehyde. The only partial oxidation which he found to give promise of commercial value, however, was the action of the silent electric discharge on mixtures of natural gas and oxygen. This produced a viscous liquid containing methyl alcohol, formaldehyde, formic acid, polymerized aldehydes, and resins. These results may well be compared with those described later in this paper on the action of ozone on methane.

A patent of Selden (56) covered the use of vanadium peroxide as a catalyst for the oxidation of methane to formaldehyde, while Wöhl (57) claimed the use of vanadic acid, molybdic acid and a number of other substances at temperatures below red heat. Müller (58) patented the preparation of formaldehyde from methane by the use at 150° of cerous cobalt nitrate as the oxidation catalyst.

The Bakelite Gesellschaft and R. Hessen (59) stated that methyl alcohol and formaldehyde might be manufactured by heating methane with excess oxygen, air, or ozonized air at red heat (600° to 1000°) under pressure in the presence of porous non-metallic inorganic contact material such as pumice, brick, earthenware fragments, highly porous slag, asbestos, quartz sand, or slag wool. Immediately after the reaction had taken place, the pressure was reduced and the methyl alcohol and formaldehyde condensed by a stream of air or gas flowing in a direction opposite to that of the hot gases. When working either at ordinary or elevated temperature, it was found advantageous to add to the catalyst, either in layers or mixed with it, substances which take up water, and give it up again at high temperatures, such as the oxides and hydrox-

ides of the alkalis or alkaline earths, magnesium or calcium chlorides, or anhydrous copper sulfate.

Nielsen (60) conducted methane over a catalyst consisting of metallic oxides at temperatures above 200°. He formulated the reactions occurring as follows:



The reaction temperatures ranged between 200° and 500°. After a short period, apparently corresponding to the consumption of a certain fraction of the oxygen present in the oxide, the reaction always stopped and the methane came over unchanged.

Nielsen and Laing (61) prepared formic acid from a gas mixture containing methane by passing it at a temperature of 250° to 800° over a metallic oxide catalyst consisting of activated copper suboxide. This was prepared by roasting in air the copper obtained by precipitating copper sulfate with zinc.

Mittasch, Willfroth and Balz (61a) claimed that the oxidation of methane is effected by passing the gas mixed with various amounts of oxygen at about 575° "over a contact mass prepared by impregnating burnt clay with a solution of boric acid, or phosphoric acid, and heating subsequently, or by mixing boric acid, or phosphoric acid, or salts of them, with diatomaceous earth and heating to red heat."

Medvedev (62) investigated the oxidation of methane by atmospheric oxygen using the phosphates and borates of tin as catalysts. The effectiveness of the borates depended upon the presence of hydrogen chloride in the reaction mixture, and their catalytic power decreased as the hydrogen chloride initially present was gradually dissipated. Medvedev showed also that in the absence of hydrogen chloride only about 2 per cent of the methane was decomposed, whereas the addition of 4 per cent of hydrogen chloride caused the decomposition of 27 per cent of the

hydrocarbon. In the presence of low concentrations of hydrogen chloride, formaldehyde was the main product, while higher concentration gave chiefly carbon monoxide. The best catalyst for the production of formaldehyde proved to be a mixture of phosphates of aluminum, tin and iron. Using this material and a gas mixture having the composition, methane 58.2 per cent, oxygen 26.1 per cent, nitrogen 8.7 per cent, hydrogen 6.96 per cent and hydrogen chloride 0.13 per cent at a temperature of 600° , methane amounting to 6.7 per cent of the total volume was decomposed, half of it being converted into formaldehyde, perhaps by the intermediate liberation of chlorine and chlorination of the methane. When a large excess of hydrogen chloride was used, about 90 per cent of the methane was converted into carbon monoxide, conditions then being favorable to maximum decomposition of formaldehyde. In order to obtain the largest yields of formaldehyde it was found advisable to carry out the oxidation in a series of communicating tubes rather than in a single tube.

In an earlier investigation on the oxidation of methane to formaldehyde, Medvedev (63) used gold, platinum, manganic oxide, nickelous oxide, aluminum oxide, cupric oxide, silver oxide, lead monoxide, and cerium dioxide catalysts on an asbestos base. Carbon dioxide alone was obtained with low rates of flow (3 liters per hour) and at low temperatures (250° to 350°). At moderate temperatures, manganic oxide was the most, and cupric oxide the least active catalyst. At temperatures, above 500° and with a rate of flow of 1 liter per minute, cupric oxide produced traces of formaldehyde and a little carbon monoxide, while the other catalysts did not. A large yield of formaldehyde was produced in the presence of glass surfaces at 600° , which was attributed to the fact that the low chemical activity of such surfaces made them unable to form peroxides. In the case of metals and their oxides, the formation of peroxides was thought to be the reason for the oxidation going farther than the formaldehyde stage. Catalysts consisting of the borates and phosphates of lead, alone or in mixtures gave the highest yields of formaldehyde at 500° to 700° . The activity of these catalysts seemed due to the presence of volatile impurities, such as lead chloride, since a long series of

experiments showed that even a small concentration of hydrogen chloride (0.13 per cent) in the gases was very beneficial in raising the yield of formaldehyde. Medvedev obtained higher yields of formaldehyde than most investigators. At 600°, from a mixture containing 13.8 per cent of methane and 17.98 per cent of oxygen with a velocity of flow of 0.23 liter per minute, the yield of formaldehydes was equivalent to 5.02 per cent of the methane passed through the apparatus.

James (63a) obtained aldehydes and acids by the oxidation of natural gas containing methane and also ethane, propane and butane in the presence of catalysts, the best of which was molybdic oxide, "but . . . other oxides and compounds of the high melting point electro-negative low atomic volume metals, such as molybdenum, vanadium, manganese, tungsten, uranium, chromium, titanium, zirconium and thorium may be used." Silver oxide could be used also as a catalyst. The oxidation reaction could be carried out at a lower temperature if the air was first passed through an ozonizer. The oxides could be mixed with each other or compounds of one metal with another could be used. With natural gas or methane molybdic oxide was most active at 550°, while the reaction was less either below or above this temperature.

The gas mixture was passed through a layer of the catalyst supported on wire gauze in an externally heated reaction vessel. At 550° the ratio of gas to air should not be over 1:3.5, and preferably 1:1. A rate of flow of 2 liters per minute was the best for the 1:1 mixture. This rate gave about one second for a molecule of the gas to pass the catalyst layer.

Formaldehyde, formic acid and water were obtained as products of the oxidation of methane. Under the best conditions the formaldehyde isolated, amounted to 6.75 per cent based on the weight of methane treated.

Schönfelder (54) found that when methane was passed with steam and air over copper or silver heated to 500°, 55 to 58 per cent of the hydrocarbon was oxidized to formaldehyde, and 10 to 20 per cent to carbon monoxide, carbon dioxide, and water, while 25 to 40 per cent remained unchanged. By the use of other

metallic catalysts, activated carbon, or the silent electric discharge, a considerable amount of formaldehyde could be obtained from methane and air, but the quantities produced were too small to make the process a commercial possibility.

Layng and Soukup (64) investigated the catalytic partial oxidation of various mixtures of natural gas, methane and ethane with oxygen by passing the mixtures through capillary tubes heated to 100° to 700°C. The solid catalysts used were mounted in the heated portion of the system while gaseous catalysts were mixed with the influent gas mixture before admitting it into the reaction chamber. After passage through the chamber the effluent gases were rapidly cooled, the intermediate products were removed by condensation and scrubbing, and the gases were then passed into a reservoir where they were accurately measured and analyzed. The initial and final gas compositions were determined by analysis in a modified Orsat apparatus.

In the analysis of intermediate products from methane oxidation, formic acid was determined by permanganate titration of residual liquors after removal of formaldehyde and methanol by distillation. Formaldehyde was determined separately in an aliquot part of the distillate obtained by neutralizing the combined condensate and wash water and removing formaldehyde and methanol by distillation. The aldehyde was determined either by the iodometric or hydroxylamine hydrochloride titration method. Methanol was estimated from the amount of standard permanganate solution required for the oxidation of both methanol and formaldehyde in another similar portion of the distillate.

Catalysts of copper and silver, their oxides, activated charcoal, platinum oxide and barium peroxide were unsatisfactory for the production of alcoholic and aldehydic intermediates on the basis of the hydrocarbon consumed and products obtained.

Oxides of nitrogen may also be used as oxygen carriers in the conversion of methane into formaldehyde. In the patent of Bibb, (65), air charged with one to two per cent by weight of nitric acid fumes, and mixed with one-fifth of its volume of methane, is preheated to about 200° and then subjected to a temperature of from 250° to 560°, preferably in a chamber containing broken pieces of

fire clay. Rapid reaction ensues, practically all the methane being converted in eight seconds into formaldehyde and other oxidation products including methyl alcohol and formic acid in minute amounts. After the removal of the products by scrubbing, the residual gases, still containing oxides of nitrogen, may be recirculated. In place of methane, natural gas may be used in the process.

Reis and Waldbauer (66) found abundant formation of formaldehyde in the flame produced by burning a mixture of methane with nitric oxide or nitrogen peroxide.

When Layng and Soukup (64) added small amounts of nitrogen dioxide to mixtures of methane and oxygen, and ethane and oxygen and passed the mixtures through heated capillary tubes, the oxidations were promoted materially by the nitrogen dioxide. Yields of oxygenated derivatives were obtained varying from fifteen to thirty per cent by volume of the amount of hydrocarbon used.

They made experiments also on a large scale with nitrogen dioxide as catalyst in order to obtain data on the character of oxygenated derivatives formed in these oxidation reactions carried out in a semi-continuous apparatus. "In a typical series of experiments, using pure methane as the hydrocarbon source, four passages of the gas through the system (adding oxygen before each pass in order to maintain a constant oxygen: hydrocarbon ratio) resulted in a yield of oxygenated derivatives amounting to 25 mgm. methanol, 205 mgm. formaldehyde, and 76 mgm. formic acid per liter (standard conditions) of methane decomposed."

Methyl nitrite in concentrations of one to two per cent exerted a promoting action less vigorous than that of nitrogen peroxide but more pronounced than that of the other catalysts investigated by Layng and Soukup under approximately similar operating conditions. The promoting action of five per cent of hydrogen chloride was less than that obtained by Medvedev (63). This difference can probably be explained by the additional contact catalysts employed by Medvedev.

Voss (67) reviewed the patents of Glock (46), Hausman (47), Bibb (65), and Plauson (68), which deal with the direct oxidation

of methane to methyl alcohol. The first three of these have been discussed earlier in this paper. Plauson used carbon dioxide as an oxygen carrier of mild action. By heating methane and carbon dioxide in the presence of such catalysts as copper, silver, and nickel, or alloys of these metals with one another or with aluminum, tin or zinc, a mixture of methyl alcohol and formaldehyde was formed. The course of the reaction depended much upon the velocity of flow of the gas mixture; a slow rate of flow favored the formation of methyl alcohol while rapid passage of the gas encouraged the formation of formaldehyde.

By the incomplete combustion of methane, Patart (69) obtained mixtures of carbon monoxide and hydrogen for use in the catalytic production of methyl alcohol and other oxygenated hydrocarbon derivatives. In this method methane was mixed with about half its volume of oxygen and injected into a mass of coke maintained at approximately 1000°. In a later patent (70), he claimed the operation of the process in such a way as to produce the gases in the ratio of two moles of hydrogen to one of carbon monoxide. This mixture was then submitted to the action of pressure and a catalyst in order to form the methyl alcohol and related products.

Yant and Hawk (71) oxidized mixtures containing approximately four per cent of methane in air to carbon dioxide and water, working through the temperature range of 150° to 350° and employing as catalysts a large number of metals and oxides, including uranium oxide, thorium oxide, cerium oxide, platinum black, nickel, platinum and nickel, copper and cobalt, cobaltic oxide, nickel oxide, and a mixture of cobaltic oxide and nickelic oxide with manganese dioxide, ferric oxide and chromic oxide. Cobaltic oxide was the most efficient catalyst while manganese dioxide and nickelic oxide were next in order of effectiveness.

Reyerson and Swearingen (72) tested the catalytic activity of metallized silica gels on the oxidation of methane. Metallic films of platinum, palladium, copper and silver were deposited over the entire surface of the gel by reduction of the respective metallic salts. Mixtures of methane and oxygen containing from 20 to 31 per cent of oxygen and also a mixture containing 73 per cent

of that gas were streamed at rates varying from 15 to 200 cc. per minute through an apparent volume of 5 cc. of catalyst at temperatures between 200° and 400°. After reaction, the gases were analyzed for carbon dioxide and oxygen, as preliminary experiments had shown that carbon dioxide was the only oxidation product formed in a sufficient amount to be detected.

In the case of the copper catalyst, apparently it was necessary for some of the copper to be oxidized before it could catalyse the oxidation. The silver catalyst consumed oxygen, probably forming silver oxide, but exerted no catalytic action on the methane. With the platinized and palladized gels there was a limited range of oxygen percentage within which marked catalysis occurred; both below and above this range the oxidation diminished. The platinized catalyst began to be active at 240° while the palladium had no effect below 330°. The platinized gel was the most active of all the catalysts.

A phase of oxidation in which catalysts are of particular importance is the preferential oxidation of gas mixtures. The large amount of work which has been done on the oxidation of hydrogen in the presence of methane by the use of palladium had already been outlined. Bancroft has summarized in two papers what is known regarding preferential oxidation of other mixtures containing methane. One of these (73) considers the influence of cupric oxide, chamotte and borosilicate glass on the combustion of mixtures of hydrogen and methane. Much of the same information is presented in the second paper (74), in which he tabulates the known data on the preferential oxidation of such gas mixtures as follows:

1. In the presence of platinum, hydrogen and ethane burn more readily than methane.
2. In the presence of copper oxide at 250°, all the hydrogen in a methane-hydrogen mixture can be burned without any of the methane being decomposed.
3. In the presence of chamotte at 500°, hydrogen burns much more readily than methane.
4. In borosilicate tubes at 300° to 400° (the work of Bone) methane combines with oxygen with an enormously greater velocity than does hydrogen, while ethane burns much more readily than methane.

5. When mixtures of methane, oxygen and hydrogen or carbon monoxide are exploded by an electric spark, the methane burns much more rapidly than the hydrogen or carbon monoxide.
6. By suitable selection of catalytic agent, it should be possible to get all stages from the complete burning of methane to the complete burning of hydrogen.
7. It seems that methane burns more readily than hydrogen at high temperatures, and in the absence of solid catalytic agents.

What little is known of the influence of radioactive material on methane oxidation is contained in two papers by Lind and Bardwell. In the first brief account of their work (75), they stated that under the influence of the alpha radiation from radon the oxidation of methane proceeded completely to carbon dioxide and water. In the later paper (76) they reported that the oxidation took place in one step, and from the numerical relation between the number of gaseous ions produced and the methane molecules oxidized, they postulated the formation of triplet ion clusters, as shown in the following reaction:



The quantities of oxidation products appearing showed that the gas ions produced 75 per cent of the oxidation theoretically possible. These workers (77) also studied the influence of anti-knock reagents and showed that in the presence of alpha radiation from radon, selenium diethyl accelerated the oxidation of methane.

d. Oxidation by ozone

A number of workers have studied the oxidation of methane by ozone. The first experimenters in this field, Houzeau and Renard (78) reported negative results at ordinary temperatures. Maquenne (79) also stated that pure methane did not react with ozone, but he found that when it was mixed with oxygen and subjected to the silent discharge, it yielded formaldehyde and formic acid. Mailfert (80), however, succeeded in oxidizing methane with ozone producing carbon dioxide, formic acid and acetic acid. Otto (81) reported that in the cold, ozone converted methane into

formaldehyde, traces of methyl alcohol and formic acid, while formaldehyde and formic acid were produced when the mixture was heated to 100°. Drugman's (82) results were very similar. He found the reaction to be very slight at 15°, but noticeable at 100°. He did not report methyl alcohol in the reaction products.

Ozone apparently does not react at all readily with methane when the hydrocarbon is in great dilution, as Urbain found (83), in searching for the cause of the disappearance of methane from the atmosphere, that in a dilution of one to one hundred, it was very difficult to separate methane from air by ozonization. After circulating the gas mixture through an ozonizer for five hours, he found that but one-third of the methane had been acted upon.

There have already been mentioned the rather incidental use of ozonized air in a patent of the Bakelite Gesellschaft (59) for the production of methyl alcohol and formaldehyde, and the experimentation with the silent electric discharge by Elworthy (13) and by Schönfelder (54).

The most extensive investigations that have been made on this method of methane oxidation are those of Wheeler and Blair (84). They passed a mixture containing three per cent of the hydrocarbon in oxygen through an ozonizer and then led it into hard glass tubes heated to various temperatures in an electric furnace. The gaseous products were washed with water and neutral potassium iodide and then collected in a gas holder over a fifty per cent mixture of glycerol in water. Formaldehyde was the first product isolated from this reaction.

These workers' results are summarized in table 5.

At all temperatures the greater portion of the methane was oxidized to carbon dioxide. No carbon monoxide was detected in any experiment. It is assumed that the ozone oxidized the formaldehyde first formed to formic acid which in turn was oxidized rapidly to carbon dioxide and water. Mixtures containing over 60 per cent of methane in oxygen gave similar results, but because the concentration of ozone was lower, less interaction occurred.

In other experiments oxygen alone was passed through the ozonizer and methane then mixed with it, in the ratio of five volumes of oxygen to one of methane before the methane entered

the reaction tube. The reaction was slightly greater than in the first experiments because of the greater concentration of methane. In the presence of catalysts, such as nickel oxide-pumice, aluminum oxide-pumice, ferric oxide-pumice, and platinized asbestos-pumice, the ozone decomposed so rapidly even below 100° that very little oxidation of the methane occurred. Methyl alcohol was not detected among the products in any of these experiments.

Ledbury and Blair (33) believe that an industrial process for the production of formaldehyde by the ozonization of methane has little prospect of success, because of the low yields of formaldehyde, as compared with the amount of ozone consumed. Fur-

TABLE 5
Ozone oxidation of methane

	EXPERI- MENT 1	EXPERI- MENT 2	EXPERI- MENT 3	EXPERI- MENT 4	EXPERI- MENT 5
Temperature of reaction tube	10°	100°	200°	300°	400°
Milligrams of formaldehyde produced per liter of mixture used.....	0.3	0.8	1.5	2.2	0.5
Formic acid.....	Trace	Trace	Trace	Trace	Trace
Carbon dioxide formed, cc. per liter of mixture used.....		5	7	6	5
Methane converted into formaldehyde, per cent.....		9	14	20	9
Ozone reacting, per cent.....	5	53	76	68	52
Ozone directly decomposed per cent.....	Nil	15	15	32	48

thermore, in a large scale circulating system such as would be required, the danger of explosion would be great.

e. Oxidation of methane by chemical reagents

Though the action of a wide variety of chemical oxidants on methane is reported in the literature, the field has not been worked intensively.

Investigators differ as to the behavior of methane with concentrated sulfuric acid. Aime (85), long ago, stated that concentrated sulfuric acid attacked the hydrocarbon with the formation of water, sulfur dioxide, and carbon. Buckton and Hofmann (86), however, reported no change even at 100°.

On passing mine gas through neutral palladium chloride, Böttger (87) obtained a black precipitate. Phillips (88) later showed, however, that methane alone did not reduce palladium chloride, either when cold or at 100°.

Mueller (89) found that methane reduced ferric oxide to the magnetic oxide at the temperature of a Bunsen flame. At higher temperatures ferrous oxide was formed. Methane reduced the red oxide of manganese, cobalt oxide, copper oxide, and bismuth oxide, the last named slowly; lead peroxide was decomposed explosively, while the oxides of zinc and tin remained unchanged. Darvydowa (90) found that methane did not react with silver oxide up to 150°. A process was patented by Blackmore (91) in which methane was heated with various metallic oxides to form methyl alcohol or formaldehyde. He claimed a yield of 125 pounds of methyl alcohol from 1500 cubic feet of methane at temperature of 127° while at 157° the same amount of methane produced 118 pounds of formaldehyde. The oxides used were ferrous-ferric oxide, cupric oxide, and manganese and barium dioxides.

Ludwig (92) reported that chromic acid had no action on methane. The acid was used in both high and low concentrations, but no change occurred during a week's contact.

Cooke (93) reported the reaction of methane with nitric oxide under the influence of an electric spark, when the volume of the hydrocarbon was "not less than one twentieth nor more than one-eighth of that of the nitric oxide used." The carbon of the methane was entirely oxidized to carbon dioxide. Bailey (94) employed oxides of nitrogen in an oxidation process, in which natural gas or some other gaseous mixture with a high methane content was mixed with two volumes of nitric oxide and sufficient air or oxygen to convert the nitric oxide into nitrogen peroxide. The mixture was then passed through a red hot porcelain tube. Formaldehyde was formed, and its further oxidation was prevented by one of the following expedients: either (1) the gases were quickly cooled by passing them through water containing calcium carbonate in suspension, the calcium carbonate at once decomposing any nitric or nitrous acid that might have formed; or (2) the hot gases were passed over a dehydrating agent such as lime,

whereby the water formed during the reaction was absorbed and the formation of acid prevented in this way. Had these acids been permitted to form, they would have oxidized the formaldehyde to carbon dioxide and water. It will be recalled that Bibb (65) and also Reis and Waldbauer (95) employed oxides of nitrogen in small proportion in oxidation processes essentially catalytic. Berl and Fischer (29) found that the combustion of methane in nitrogen peroxide produced formaldehyde.

Lang (96) stated that between 700° and 800° methane began to reduce carbon dioxide with the liberation of carbon, while the formation of carbon monoxide from these two gases was brisk at 950° to 1054° . The reaction of methane with water vapor at high temperature yielded carbon monoxide and hydrogen in the presence of an excess of water, while under other conditions much carbon was formed.

According to a patent by H. Otto Traun's Forschungs-Laboratorium (97), the oxidation of methane to formaldehyde and methyl alcohol was effected by momentarily heating the hydrocarbon with carbon dioxide. Heat decomposed the carbon dioxide and gave nascent oxygen which, under suitable conditions, produced much methyl alcohol and formaldehyde, but only a little formic acid. The process could be carried out by passing the mixture of gases through a constricted tube which was heated at the constriction. Slow passage of the gas favored the formation of methyl alcohol while rapid passage favored the production of formaldehyde. The tube in which the gas was heated was made of copper, silver, nickel or alloys of these metals or alloys with aluminum, tin, or zinc, and acted catalytically in promoting the reaction. The tubes could also be made of iron or steel, in which cases small quantities of copper, silver, aluminum, nickel or their alloys were useful in the form of turnings or wire within the iron or steel tubes.

Dreyfus (98) found that acetic acid, acetone, or mixtures of these were made by passing methane together with carbon monoxide or carbon dioxide under pressure and at temperatures below 500° , over a catalytic material such as copper, iron, nickel, cobalt, palladium black, platinum black, nickel carbonate or other

metallic carbonate which decomposed at temperatures below 500°. The rate of passage of the mixed gases over the catalyst depended upon the temperature and pressure. Pressures of 12 to 50 atmospheres and temperatures of 120° to 300° could be used, under which conditions the speed of the gas mixture was from 1 to 20 liters per minute.

Phillips (88) reported a lengthy series of experiments with methane and a number of oxidizing agents. Potassium permanganate in 2 per cent solution, either neutral or acidified with sulfuric acid was not affected by this hydrocarbon nor was potassium ferri-cyanide changed. However, when methane was conducted into strong sulfuric acid containing solid potassium permanganate, immediate oxidation occurred. Osmic acid was unaffected in the cold, while potassium ruthenate was slowly reduced to metallic ruthenium. Hydrogen peroxide mixed with lime water remained clear when in contact with this gas while calcium hypobromite precipitated no carbonate. Dehn (99) later reported that sodium hypobromite also was without effect on methane even after standing with it for several months.

At elevated temperatures methane reduced ferric oxide with the formation of carbon monoxide and carbon dioxide. Iodic acid (in crystal form) was not reduced on heating nearly to its dissociation temperature nor was iodic pentoxide attacked at any temperature up to its point of decomposition. Nickel chloride, though it had no apparent effect on methane, was changed in its crystal form by exposure to this gas at low temperature. At higher temperature a peculiar crystalline mass was formed, which at low red heat decomposed with reduction of the metallic salt and separation of carbon.

V. Meyer and Saam (100) found that methane was very slowly oxidized on shaking with a five per cent solution of potassium permanganate. The oxidation was more rapid than in the case of ethane.

An English patent was granted to Lance (101) for a method of preparing methyl alcohol from methane by the use of hydrogen peroxide, with or without ferrous sulfate or monopersulfuric acid, or by the use of monopersulfuric acid alone. A similar process

was claimed by Lance and Elworthy (102) in a French patent, which also included the production of formaldehyde.

Hoffman and Schneider (103) found that a small amount of methane was absorbed by chlorate solutions in contact with certain metals in finely divided form. On using platinum there was measurable absorption while with rhodium and palladium there was some evidence, but no conclusive proof of reaction. All of the other noble metals were tried without any absorption occurring. These authors were able to separate hydrogen from mixtures with methane by absorption methods.

Berl and Fischer (29) found that oxidation of methane with sulfur dioxide produced no formaldehyde, while by the action of sulfur trioxide under optimum conditions 0.5 per cent of formaldehyde was formed.

f. Oxidation by bacteria

Several investigators have published papers on the bacterial oxidation of methane. Although this phenomenon is apparently common, only a few of the organisms bringing it about have as yet been identified.

Kaserer (104) found that methane was oxidized by the microorganisms of the soil, and that they also consumed hydrogen. He noticed that nitrification was hindered by the presence of hydrogen or methane, as these gases were utilized by the bacteria in preference to nitrogen.

Söhngen (105) and also Urbain (83) observed that mixtures of methane and oxygen were slowly oxidized in the presence of green plants, probably because of bacteria introduced with the plants. Later Söhngen (106) described a bacterium (*Bacillus methanicus*) which oxidized methane when that hydrocarbon was mixed with two volumes of air.

Giglioli and Masoni (107) also studied the biological removal of methane from gas mixtures. They found the optimum temperature for this process to be 30°. In studying the distribution of the organisms which in the presence of oxygen consumed methane, they found that the deeper layers of the ground contained more of them than the surface layers, and that they were abundant in the slime of rivers and in dungheaps.

Harrison and Aiyer (108) showed that the organized film overlying the surface of swamp rice and paddy soils was capable of oxidizing methane to carbon dioxide and water. Aiyer (109) later identified the organisms responsible for the oxidation as *B. fluorescens liquefaciens*. In culture, this bacterium was able to oxidize considerable portions of methane only as long as it was propagated on purely mineral media. In the presence of much organic matter, its power to oxidize methane was markedly reduced.

3. THE OXIDATION OF ETHANE

a. General

By reason of the larger number of products theoretically possible, the oxidation of ethane is an even more complex process than that of methane. The products obtained and their proportions vary widely with the different methods and the conditions of oxidation.

Slow oxidation of ethane in sealed borosilicate glass bulbs at a pressure of 1.75 to 2.33 atmospheres produces a gaseous mixture consisting of carbon monoxide, carbon dioxide, methane, free carbon, and water vapor, while the circulation of mixtures of ethane and oxygen at reduced pressure with continuous removal of the products yields carbon monoxide, carbon dioxide, hydrogen, ethylene, formaldehyde, acetaldehyde and water, with some indications of the formation of formic acid.

The explosion of mixtures of ethane and oxygen produces considerable amounts of unsaturated hydrocarbons, whose proportion increases as the initial pressure of the mixture is diminished. The products which have been identified are carbon monoxide, hydrogen, methane, ethylene, acetylene, and water vapor.

The presence of ethyl alcohol has not been established in the products of oxidation by any of these means mentioned above, but it is produced when the oxidation is effected by means of ozone. Acetaldehyde, acetic acid, and traces of hydrogen peroxide are also formed by this method.

The reactions producing this variety of products, as formulated by Bone on the basis of his hydroxylation theory, are summarized in table 3.

b. Oxidation by oxygen and air

The incomplete combustion of ethane was investigated first by E. von Meyer (110). He found that a large excess of oxygen was required to produce ignition when ethane was mixed with hydrogen and oxygen. The oxidation of ethane by oxygen was also studied by Berthelot and Vieille (111), who compared the pressures produced in a number of gas reactions. They found that when one mole of ethane interacted with seven moles of oxygen, a pressure of 16.18 atmospheres was developed by the explosion, about the same pressure as that developed by the rapid combustion of other saturated and unsaturated hydrocarbons.

According to Schlegel (112) the combustion of ethane in the presence of oxygen and chlorine takes place in accordance with the following equation:



Thus there is preferential reaction of the hydrogen with chlorine.

Bone and Stockings (113) observed that under similar conditions, ethane burns much more rapidly than methane. In borosilicate glass bulbs both hydrocarbons were oxidized considerably below 400°. There was apparently no preferential combustion of either hydrogen or carbon when ethane reacted in these bulbs at 250 to 400° under pressures of 1.75 to 2.33 atmospheres with a quantity of oxygen insufficient to burn it to carbon monoxide and water. Carbon monoxide, carbon dioxide, oxygen, methane, and ethane were among the end products.

When the oxidation of similar mixtures of ethane and oxygen was carried out under reduced pressure by continuously circulating the gases through a tube kept at 400° to 500°, the gaseous products included carbon monoxide, carbon dioxide, hydrogen, ethylene, oxygen, and ethane. Both formaldehyde and acetaldehyde were detected in the water through which the gases passed immediately after leaving the heated tube. There was also some evidence of the intermediate formation of formic acid.

Bone and Wheeler (16), following their work on methane with studies on ethane oxidation, obtained additional experimental evidence for the hydroxylation theory.

Bone and Drugman (5) found that equimolecular mixtures of ethane and oxygen, when exploded in a closed borosilicate glass bulb, formed carbon monoxide, hydrogen, methane, acetylene and ethylene. The quantities of unsaturated hydrocarbons, as well as of water, in the final products showed a tendency to increase as the initial pressure diminished. It is worthy of note that these workers detected aldehydes in the products of the burning of oxygen in ethane and also in the interconal gases of an ethane flame.

In other experiments, it was found that acetaldehyde decomposed at about 400° into methane and carbon monoxide while at higher temperatures it formed hydrogen, methane, carbon monoxide and free carbon. The presence of all of these substances together with steam in the products of the explosion of mixtures of ethane and oxygen was pointed out as being in conformity with the assumptions of the hydroxylation theory.

The relative rates of oxidation observed at low temperatures with mixtures containing varying proportions of oxygen were interpreted as showing that the monohydroxy—and not a dihydroxy—derivative was formed initially. It seemed to these authors that it was the oxygenated molecule which decomposed in a flame and not the original hydrocarbon.

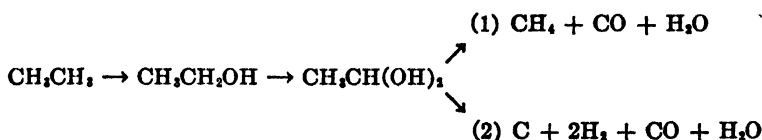
Bone, Drugman and Andrew (4) found that the lower the pressures at which a glass globe was filled with ethane, mixed with an amount of oxygen insufficient for its combustion to carbon monoxide and water, the greater was the quantity of water, aldehydes and unsaturated hydrocarbons produced when the mixture was fired. In accordance with Bone's ideas, these results would indicate that water, unsaturated hydrocarbons and aldehydes were produced during the initial stages of combustion while carbon was a later product.

The results obtained by the detonation of mixtures of ethane and oxygen in a coil of lead tubing 20 feet long indicated that no preferential combustion of carbon or hydrogen occurred in the explosions. After the explosion of an equimolecular mixture of ethane and oxygen, the products included acetylene, ethylene, methane, and hydrogen, besides water, carbon monoxide, carbon dioxide, and free carbon. The rinsings of the explosion chamber

gave a strong aldehyde reaction with Schiff's reagent. These workers considered the mechanism of combustion to be essentially the same in both detonation and inflammation.

In later work, Bone (114) exploded other mixtures of ethane and oxygen, and always found in the products of the reaction substances of aldehyde nature which were recognized by the use of Schiff's reagent.

Bone, Davies, Gray, Henstock and Dawson (115) studied the explosion of ethane with an equal volume of oxygen and represented the reaction as taking place in the following steps:



Andrew (116) extended his study of the water gas equilibrium to the mixtures, $2\text{C}_2\text{H}_6 + 3\text{O}_2$ and $2\text{C}_2\text{H}_6 + 5\text{O}_2$, which on ignition in a spherical vessel or in a coil gave carbon dioxide, carbon monoxide, hydrogen, water vapor, methane, acetylene, and ethylene. The yields of carbon and of aldehydes showed wide variation, depending on the type of vessel used.

Marks (116a) found that formaldehyde could be produced with greater ease by the partial oxidation of ethane than was the case with methane. He passed a mixture containing one volume of ethane and two volumes of air at a rate of 27 liters per hour through a silica tube 0.5 inch in diameter heated to 700 to 710° over a length of 2 feet. The exit gases were divided into two streams so that ten volumes of exit gas were recirculated with each volume of fresh mixture. The liquid condensed in the cooled receiver consisted of an aqueous solution of formaldehyde. Formaldehyde was formed in the amount of 8.5 pounds per thousand cubic feet of ethane treated; 1.4 pounds of acetaldehyde being produced simultaneously. The formaldehyde produced amounted to 7.4 per cent of the ethane treated. Some of the ethane decomposed and gave 33.4 per cent of ethylene during the reaction.

Propane and butane or higher paraffins may be used with simi-

lar results. The ease with which the paraffin hydrocarbons oxidize increases with their molecular weight.

Catalysts such as heavy metals and their compounds were found to be useless in the oxidation reactions of the paraffin hydrocarbons tried by Marks.

c. Catalytic oxidation

Phillips (117) studied the conditions for the oxidation of ethane (3.1 per cent in a mixture with air) in the presence of palladium asbestos. He found that the "lowest initial oxidation temperature," was high, being 450° for ethane while for hydrogen it was 20°. He did not state the nature of the oxidation products.

Richardt (43) studied the combustion of ethane mixed with other gases in the presence of palladium wire. He found that mixtures of methane and ethane were difficult to separate by the use of platinum or palladium, but that if hydrogen was present, it might be removed from the mixture by fractional combustion.

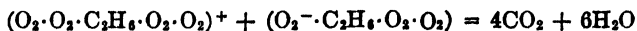
Acetaldehyde, acetic acid, and ethyl alcohol are given by Glock (118) as the products of his patented process for the oxidation of ethane with air using pumice, asbestos, or copper as catalytic agents.

The I. G. Farbenindustrie Akt-Ges. (28) obtained ethane by adsorption with active charcoal or silica from the gas produced by low temperature carbonization of bituminous material, and subjected it to incomplete combustion. The hydrocarbon was passed, with oxygen, through a porcelain tube filled with fragments of pumice and heated to 900°. They claimed that the products contained over 25 per cent of ethylene.

Bancroft (73), discussed the preferential catalytic combustion of ethane and concluded, on the basis of Bone's data, that ethane as well as methane burns more rapidly than either hydrogen or carbon monoxide in borosilicate bulbs at 300° to 400°.

Under the action of alpha radiation from radon, ethane was completely oxidized in one step in the experiments of Lind and Bardwell (75, 76). In the initial stages the reaction between ethane and oxygen was nearly twice as fast as in the case of methane, but the velocity decreased sharply when the reaction was

about 70 per cent complete. The assumed groupings of ethane and oxygen molecules about the gaseous ions were as shown in the following equation:



As in the case of methane, the yield of oxidation products was 75 per cent of the maximum theoretically possible on the basis of the total number of ions present.

d. Oxidation by ozone

The work of Bone and Drugman (119) on ozone oxidation of ethane is of great importance from a theoretical standpoint, and it possesses some industrial interest as well. They obtained ethyl alcohol by the interaction of ethane and ozone at 100°. In their experiments ethane and ozonized air (ozone 2.33 per cent) were led separately into the top of a wide vertical glass tube, about 18 inches long, packed with glass beads and heated by a steam jacket. The proportion of the gases was so regulated that the ethane was always present in large excess. Under these conditions the ozone disappeared entirely as the mixture descended the tube. The gases were then drawn through a series of cooled glass worms containing water for the absorption of soluble products. Each experiment extended over three or four days, during which time about 4 liters of ethane and 13 to 15 liters of ozonized air passed through the apparatus. Examination of the liquid from the condenser showed that ethyl alcohol, acetaldehyde, acetic acid, and traces of formaldehyde were present. An examination of the gaseous products showed that they did not contain acetylene, ethylene or free hydrogen.

In further work the interaction of ethane with oxygen containing 10 per cent of ozone was studied by Drugman (82). The oxidation was slow at 15°, although much faster than in the case of methane. The products obtained were ethyl alcohol, acetaldehyde, and acetic acid, besides traces of hydrogen peroxide. At 100°, using a large excess of ethane, the reaction was more rapid and much less acid was formed. Acetaldehyde was the main product of the reaction, though traces of hydrogen peroxide were also

formed and ethyl alcohol was produced in larger quantities than at the lower temperature. Drugman made the statement: "It is clear, then, that ethyl alcohol is the first stage in the oxidation process, and that acetaldehyde and acetic acid are secondary products of the reaction."

e. Oxidation by chemical reagents

The information available on the chemical oxidation of ethane is extremely fragmentary.

Phillips (117) found that potassium ruthenate was slowly reduced to the metal by ethane and by other hydrocarbons, that potassium permanganate produced some carbon dioxide when treated with ethane, and that iodine pentoxide was not attacked up to its dissociation temperature.

Meyer and Saam (100) reported that the oxidation of ethane by 5 per cent potassium permanganate was less rapid than that of methane.

4. THE OXIDATION OF PROPANE

Incomplete as is our knowledge of the oxidation of methane and ethane, it is yet far superior to that regarding the oxidation of the higher gaseous hydrocarbons, propane, butane, isobutane, and 2,2-dimethyl propane. The literature offers but a few scattering references on these members of the series.

The combustion of propane in the presence of chlorine, was found by Schlegel (112) to lead to the formation of carbon dioxide and hydrogen chloride:



In this case, as with ethane and methane, the chlorine reacted preferentially with the hydrogen and the carbon with the oxygen.

Bone and Drugman (5) investigated the combustion of propane with oxygen by exploding two volumes of the hydrocarbon with three of oxygen in a closed tube. They found as products of the reaction: aldehydes, carbon monoxide, carbon dioxide, methane, unsaturated hydrocarbons (including acetylene), and hydrogen.

Phillips (117) found, by studying the slow oxidation of propane

in the presence of palladium asbestos and air, that the ignition point of a mixture containing 3.1 per cent propane was between 339° and 383°. He reported also that palladium chloride and potassium ruthenate were reduced by propane as they were by methane. Acidified permanganate produced some carbon dioxide from propane. Iron oxide was reduced by the hydrocarbon at elevated temperatures.

Lind and Bardwell (76) found that the oxidation of propane did not ordinarily go to completion under the influence of the alpha radiation from radon. Liquid products other than water indicated incomplete oxidation. The oxidation of propane could be brought to completion, however, by prolonged exposure to alpha radiation.

5. THE OXIDATION OF BUTANE

The substances which have been identified as products of the combustion of butane in oxygen include aldehydes, carbon monoxide, carbon dioxide, water, methane, ethylene, acetylene, hydrogen and carbon. Schlegel (112) found that the oxidation of butane in an excess of a mixture of chlorine and oxygen took place according to the equation:



Bone and Drugman (5) exploded mixtures of butane with oxygen and reported the formation of aldehydes, methane, unsaturated hydrocarbons including acetylene, carbon monoxide, water, hydrogen and carbon.

On exploding a mixture of 34 per cent butane and 60 per cent oxygen, Bone, Drugman and Andrew (4) obtained as gaseous products: carbon monoxide, carbon dioxide, methane, ethylene, acetylene and hydrogen. They considered the hydroxylation theory to account satisfactorily for these products.

In 1849 Frankland (120) reported that butane, mixed with 50 per cent of oxygen and conducted over spongy platinum, remained unchanged at ordinary temperature, but upon gentle heating, the platinum became incandescent and with the oxidation of the butane, water and carbon were formed.

Lind and Bardwell (76) observed, as in the case of propane, that the oxidation of butane under the influence of alpha radiation from radon was not complete; the appearance of liquid products other than water indicated but partial oxidation.

Reference has been made to the application of the catalytic oxidation process of James (63a) and of Marks (116a) to propane, butane, and even higher paraffin hydrocarbons.

6. THE OXIDATION OF ISOBUTANE

Experiments of Meyer and Saam (100) showed that when isobutane was agitated with a 5 per cent solution of potassium permanganate for an hour, the amount of oxidation was scarcely perceptible.

The oxidation of isobutane in the presence of palladium asbestos was reported by Phillips (117). A mixture of 3.1 per cent of isobutane with air burned at 200° to 250°. Similarly a 3.1 per cent mixture of isobutane and air was oxidized at 214° to 250° on being passed over ruthenium asbestos. The products of the combustion included water and carbon dioxide; olefines could not be detected.

7. THE OXIDATION OF 2,2-DIMETHYL PROPANE

No reports of work on the oxidation of 2,2-dimethyl propane have appeared in the literature.

8. SUMMARY OF THE SUBSTANCES PRODUCED BY THE OXIDATION OF METHANE, ETHANE, PROPANE, BUTANE AND ISOBUTANE

A recapitulation of all of the substances which have been found as products of the oxidation of the gaseous paraffins is given in table 6. The blanks in this table, to a considerable extent, indicate gaps in our knowledge rather than the proven nonformation of the listed substances.

9. SUGGESTED PROBLEMS FOR FURTHER RESEARCH

There can be no doubt that the oxidation of the gaseous paraffin hydrocarbons is a subject of rich promise about which far too little is known. The mechanisms of the many sided reactions,

are, to say the least, highly uncertain. The experimental data are in many cases conflicting, indicating that all the conditions affecting the experiments have not been taken into account or accurately described by the various investigators. Apparently there are equilibria involved, inviting studies in kinetics. The oxidation of the gaseous hydrocarbons in the presence of hydrogen

TABLE 6

Substances identified as oxidation products of methane, ethane, propane, butane and isobutane

	METH- ANE	ETHANE	PROPANE	BUTANE	ISOBUTANE
Methyl alcohol.....	Yes				
Ethyl alcohol.....		Yes			
Formaldehyde	Yes	Yes			
Acetaldehyde.....		Yes			
"Aldehydes".....			Yes	Yes	
Formic acid.....	Yes	Yes			
Acetic acid.....		Yes			
Methane.....		Yes	Yes	Yes	
Ethylene		Yes		Yes	
Acetylene		Yes	Yes	Yes	
"Unsaturated" hydrocarbons.....			Yes	Yes	No olefins
Carbon monoxide	Yes	Yes	Yes	Yes	
Carbon dioxide	Yes	Yes	Yes	Yes	Yes
Carbon.....	Yes	Yes	Yes	Yes	
Hydrogen.....	Yes	Yes	Yes	Yes	
Water.....	Yes	Yes	Yes	Yes	Yes
Hydrogen peroxide.....		Trace			

so as to show preferential oxidation has been studied just enough to indicate its interest and complexities. The investigation of the action of chemical oxidants has but begun, while little attempt has been made to accelerate or retard the chemical oxidation of the gaseous paraffins by catalytic means. There is particular need for more study of the oxidation reactions of propane, the butanes and 2,2-dimethyl propane.

The following problems are suggested as offering opportunities for investigation:

A. Mechanism and course of the reactions

1. Investigation of the dissociation of the gaseous paraffins during oxidation.
2. Work on the mechanism of formation of unsaturated hydrocarbons in oxidation reactions.
3. Determination of the order in which alcohols, aldehydes, hydrogen, carbon monoxide, carbon dioxide, and free carbon are formed in the oxidation reactions.
4. Comparison of the steps and mechanisms of the following types of oxidations.
 - a. Slow oxidation with air or oxygen.
 - b. Explosive combustion.
 - c. Oxidation by means of ozone.
 - d. Catalytic oxidation.
 - e. Oxidation by use of chemical oxidizing agents.
5. Study of the oxidation of the gaseous paraffins by mixtures of chlorine or other halogens with oxygen, air and ozone respectively.
6. Comparison of the oxidation of n-butane and of isobutane.

B. Equilibria and kinetics

1. Investigation of the reversibility or irreversibility of the steps in the oxidation reactions.
2. Study of the equilibria produced by the reversible reactions and the shifting of these equilibria by variations in temperature, pressure and time.
3. Observation of the effects of temperature and pressure on the velocities of single oxidation reactions.

C. Catalytic oxidation and preferential combustion

1. Study of the rates of oxidation of single hydrocarbons in mixtures with other gases and of hydrocarbons themselves in admixture as influenced by temperature, pressure and catalysts.
2. Effect of the presence of knock suppressing and also of knock inducing substances on the rates of oxidation of the gaseous paraffins.
3. Influence of traces of water on the rate and course of the oxidation reactions. Is the presence of water essential to the oxidation of these hydrocarbons?

4. The retardation by catalysis of some or all of the reactions occurring in a given oxidation process.

5. Simultaneous dehydrogenation, condensation, and oxidation by employment of zinc chloride, carbon, metals, or metallic oxides as catalysts. Also use of metals such as copper, cobalt, nickel, iron, platinum, and palladium in finely divided condition together with oxides such as the lower oxides of manganese, tin, uranium, molybdenum and vanadium, in anhydrous form, which Sabatier and his associates found effective in the dehydrogenation of alcohols.

6. Determination of the function of hydrogen chloride in promoting the oxidation of methane in the presence of the borates of tin.

7. Investigation of the results of producing oxidation by passing a hydrocarbon mixed with air or oxygen through a bath of molten metal.

8. Endeavor to catalyse a specific reaction without accelerating others going on simultaneously.

D. Chemical oxidation

1. Extension of the work which has been done on the chemical oxidation of methane to its higher homologues, and the testing of other oxidizing agents, such as chromyl chloride and the oxides of chlorine.

2. Determination of the effect of catalyst promoters and demoters.

3. Obtaining data on the effects of temperature, pressure and time on chemical oxidation, in the gas phase using oxides of nitrogen or other gaseous oxidants.

4. Use of air or oxygen with higher concentrations of nitrogen, hydrogen or carbon dioxide at high pressures.

5. Oxidation under controlled temperatures, low or high, with or without electrical discharge.

6. Oxidation of the gaseous paraffin hydrocarbons while in liquid state.

7. Experimental work on the oxidation of these hydrocarbons under the influence of radiant energy, especially infra-red and ultra-violet, and perhaps x-ray radiation.

8. Determination of the influence of alpha radiation on the oxidation of isobutane and 2,2-dimethyl propane.

E. Bacterial oxidation

1. The isolation and classification of the effective organisms.

2. Study of the influence of oxygen and other gases on the methane consuming bacteria.

3. Investigation of the oxidizing action of bacteria on ethane, propane, the butanes and 2,2-dimethyl propane.

F. Problems of possible commercial value

1. Evaluation of the many patents for the preparation of formaldehyde and of the process for oxidation of methane in the presence of ammonia to form hexamethylene tetramine.

2. Preparation of alcohols by properly controlled catalytic oxidation of the gaseous paraffins or perhaps of olefins resulting from the thermal decomposition of the paraffins.

3. Investigation of the action on the gaseous paraffins of ozone formed at low temperatures by the action of the silent electric discharge on mixtures of these hydrocarbons with oxygen or on such mixtures diluted with nitrogen or with some other inert gas.

4. Oxidation in the gas phase in the presence of oxides of carbon, nitrogen, sulfur and halogens.

5. Use of vanadium pentoxide, vanadic acid, molybdic acid, and a number of other substances not yet thoroughly investigated as oxidation catalysts.

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CONTRIBUTIONS OF X-RAY STUDIES OF CRYSTAL STRUCTURE TO ORGANIC CHEMISTRY¹

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THE CARBON ATOM

Ever since the first structural formula was written, it has been the creed of organic chemists that the properties of the materials with which they work must be attributed to the shapes and sizes of their component atoms and to the arrangement of those atoms in space. Structural formulas represent hypothetical configurations of atoms which are consistent with the results of chemical and physical experiments. Because these structural formulas show an atomic configuration in only two dimensions, they have been universally recognized as being only workable fictions which, however well they may represent the chemical properties of substances, have no necessary relation to the true positions of the atoms in the molecules. In a few cases, attempts have been made to include the third dimension. Outstanding examples of this are found in the three-dimensional formulas assigned to methane and ethane on the basis of a tetrahedral carbon atom, and in the stereo-formulas of the three kinds of tartaric acid. Even such formulas have been recognized as being only figures of speech which do not necessarily correspond to the actual configuration of the atoms in space. The x-ray study of crystal structure is gradually laying the foundation for a new set of three-dimensional structural formulas. These are of such a sort, and are backed by such strong experimental evidence that we feel justified in accepting them as representing a close approximation to reality.

¹ Delivered before the Division of Organic Chemistry of the American Chemical Society at the Seventy-third Meeting, Richmond, Virginia, April 14, 1927.

The arrangement of carbon atoms in diamond (1) (2) (3) is well known. This arrangement is easiest accounted for on the basis of a tetrahedrally shaped carbon atom (4) (5). The arrangement of atoms in graphite (2) (6) (7) (8) (9) (10) is such that the "domains" (5) or "packing shapes" of the carbon atoms are to be regarded as being very nearly tetrahedral. This is in complete agreement with all the chemical evidence, and we may consider the organic chemist's picture of a tetrahedral carbon atom to be on a sure foundation. There is no clue, however, as to whether the four valence electrons of the carbon atom are "attached" at the vertices of the tetrahedral atomic domain, or at the centers of the faces, (fig. 1). The reason for this lies in

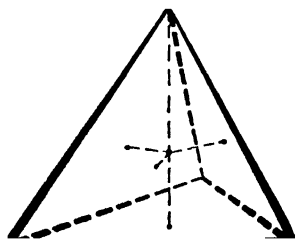


FIG. 1. TETRAHEDRAL SHAPE OF THE CARBON ATOM

the fact that the angles subtended at the center by the vertices of the tetrahedron are the same as the angles subtended by the face-centers, $109^{\circ} 28'$. It is only a matter of words, therefore, whether we say that the four valence electrons have mean positions at the centers of the faces of a given tetrahedron, or whether we say that their mean positions lie at the vertices of a second tetrahedron inscribed in the first so that the four vertices of the second tetrahedron coincide with the centers of the four faces of the first. The essential thing is that carbon atoms pack in crystals practically as though they were tetrahedra, i.e., they have four points $109^{\circ} 28'$ apart which can not be distinguished from each other. The distance of closest approach of carbon atoms in diamond is 1.54×10^{-8} cm. In graphite it is 1.50×10^{-8} cm. In order to make certain of the illustrations in this

article (figs. 4, 7, 8, 9 and 10) appear more stereoscopic, the carbon atoms will be represented by circles the radii of which correspond to 0.75×10^{-8} cm. The interpretation of these circles in terms of tetrahedra will in all cases be sufficiently obvious.

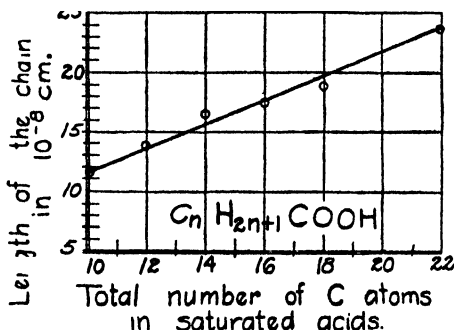


FIG. 2. LENGTHS OF MOLECULES OF SATURATED FATTY ACIDS (MÜLLER)

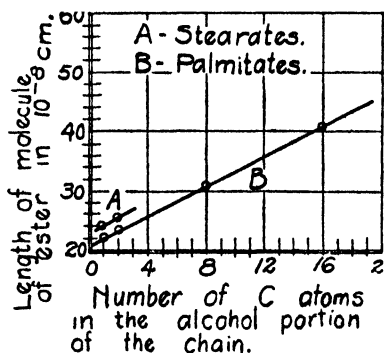


FIG. 3. LENGTHS OF MOLECULES OF ESTERS OF PALMITIC AND STEARIC ACIDS (SHEARER)

THE PARAFFIN SERIES

The ordinary structural formulas for the paraffins, and for the acids and esters derived from them, show the carbon atoms as lying along a straight line. Such a picture is not consistent with the x-ray data. For each of the saturated fatty acids and their esters, the x-ray diffraction patterns show three dimensions. Two of these are, within experimental error, identical for all the compounds so far tested (11) (12) (13) (14) (15) (16).

The average numerical values are 4.1 and 3.7×10^{-8} cm. The third dimension varies rather systematically with the number of carbon atoms in the molecule. The interpretation of all this is taken to be that all the saturated acids, and their esters, in the paraffin series have essentially the same cross section, but that the length of the "chain" depends upon the number of carbon atoms in it. The cross section is greater than would be expected

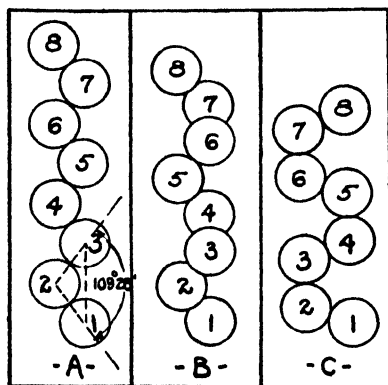


FIG. 4. THEORETICALLY POSSIBLE CARBON CHAINS (MÜLLER AND SHEARER)

A corresponds to the saturated alcohols. C corresponds to the free saturated acids.

on the basis of a straight chain of carbon atoms each 1.5×10^{-8} cm. in "diameter." It is hard to imagine that the hydrogen atoms (the smallest in the whole list of elements) could account for the discrepancy in cross section. It seems necessary to assume that the carbon chain is in zig-zags. This assumption is strengthened by the fact that the chains are considerably shorter than the distances calculated by multiplying the "diameter" of carbon by the number of carbons in the chain. The lengths found experimentally by Müller (11) for the chains of various acids are given in figure 2.²

² Langmuir (17) measured the lengths of the molecules of palmitic and stearic acids in terms of their spreading on water. His values are 11 per cent higher than those of Müller by x-ray methods. Adam's values (18) for myristic and behenic acids are 13 per cent higher. This is perhaps as close agreement as might be expected because of the experimental conditions inherent in the water spreading method.

Similar data by Shearer (12) for the lengths of the molecules of various esters of palmitic and stearic acids are given in figure 3. The data show that the increase in the length of the alcohol averages $1.22^5 \times 10^{-8}$ cm. for each CH_2 group. This is to be contrasted with an average increase of 1.02×10^{-8} cm. per CH_2 group for the free fatty acids of figure 2.

Müller and Shearer (13) have investigated the effect of possible configurations of carbon atoms on the length of the chain. Their three simplest cases are shown in figure 4. In A all the carbon atoms lie in one plane. The arrangement is identical with that chain of atoms in diamond in the 1 1 0 plane which runs parallel to the 1 0 0 plane. Since the atoms are tetrahedral in shape, the angle 1 2 3 is taken as $109^\circ 28'$. The distance 1 2 or 2 3 is equal to the "diameter" of carbon, i.e., 1.50×10^{-8} cm. The vertical length along the chain which is contributed by each carbon atom is half the distance 1 3. It is

$$1.50 \times 10^{-8} \sin \frac{109^\circ 28'}{2}$$

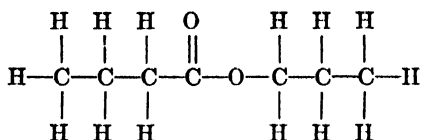
or 1.22×10^{-8} cm. This agrees with the experimental value for the average increase per carbon atom for the alcohols, as measured in the esters of saturated acids. It is therefore assumed that the carbons in the chains of saturated alcohols have the configuration of figure 4A. It should be noted that the model requires all the carbons to produce the same increment in length. This agrees with Figure 3 which gives, on a single straight line, data for both odd and even numbered alcohols.

B of figure 4 represents a spiral of tetrahedral carbon atoms. It is evident that it does not represent the experimental facts for the increment in length per atom is 1.12×10^{-8} cm. which is about half way between the correct values for the alcohols and for the saturated fatty acids. Although this configuration is theoretically possible for carbon atoms, it does not appear in either diamond or graphite.

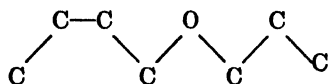
C of figure 4 shows a third possible configuration which actually occurs in diamond. Atoms 1, 2 and 3 are related to each other as in figure 4A. Atoms 4, 5, and 6 are also like the corresponding

atoms in figure 4A but atom 4 is joined on to a different tetrahedral face of 3 in C than in A. Each pair of atoms contributes 2.0×10^{-8} cm. to the length of the chain. The average increment in length per atom, 1.0×10^{-8} cm. is within experimental error identical with the average increment per atom for the saturated fatty acids of figure 2. Of each pair of atoms in figure 4 C, one contributes 1.5×10^{-8} cm. and the other contributes 0.5×10^{-8} cm. This again agrees with the experimental facts, for if the lengths of the odd numbered acids were plotted in figure 2 their graph would have been parallel to the length of the even numbered acids, but a little above it. "The difference between the acids containing an odd and an even number of carbon atoms is interesting. It is well known that similar differences are found in their melting points. Also the even-numbered acids are common in nature, whilst the odds are very rare. It would therefore appear that there is a stronger tendency to add two carbon atoms to the acid chain than only one (13)."

The x-ray investigation of the paraffin series, in so far as structural formulas are concerned, may be illustrated in terms of an ester like propyl butyrate. The ordinary structural formula is



If the interpretation of Müller and Shearer is correct, the carbons should be written

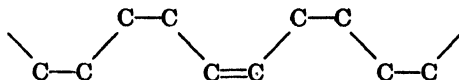


The end carbons have three H atoms attached at angles $109^\circ 28'$ from the line joining the end carbon to its next neighboring carbon. In the same way the hydrogen atoms of the CH_2 groups would be one above and one below the plane of the paper at angles determined by the tetrahedral carbon atom. The

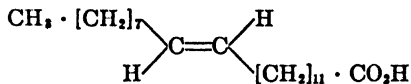
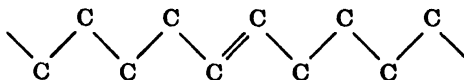
additional oxygen atom of the carboxyl group would likewise not lie in the plane of the paper.

There is one other important result of the x-ray investigation of the fatty acids that deserves mention. The x-ray data show that both the saturated and the unsaturated acids have their molecules in pairs as though the two CO-OH groups were in contact. In other words the natural state of these acids, when free from water,

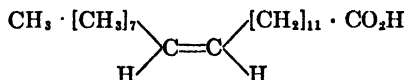
Portion of the Carbon Chain of ERUCIC ACID.



Portion of the Carbon Chain of BRASSIDIC ACID.



Ordinarily called Erucic Acid,
Actually BRASSIDIC ACID.



Ordinarily called Brassidic Acid,
Actually ERUCIC ACID.

FIG. 5

is one of association, with n equal to 2. In this connection it is interesting to remember that the molecular weight of acetic acid, measured in terms of the depression of the freezing point of benzene is *twice* the formula weight. There is no x-ray evidence for any association of the esters.

Very little is known, from the x-ray standpoint, of the unsaturated fatty acids. Müller and Shearer have investigated the

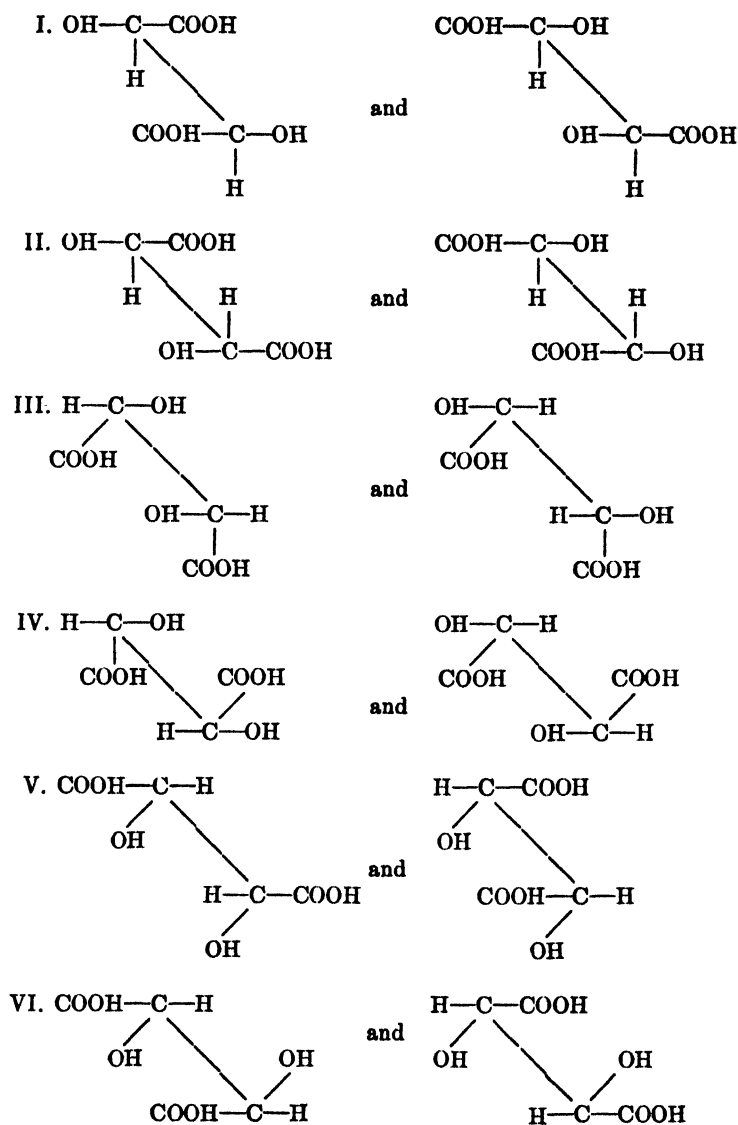


FIG. 6. POSSIBLE MOLECULAR STRUCTURES OF DEXTRO- AND LAEVO-ROTARY TARTARIC ACID PERMITTED BY THEIR CHEMICAL PROPERTIES (ASTBURY)

two isomers, erucic acid and brassidic acid. Each of these contains 22 carbon atoms. There is one double bond, similarly placed, in each acid. The x-ray results are consistent with the structural formulas of figure 5. Since the material ordinarily known to organic chemists as brassidic acid has a chain 12×10^{-8} cm. longer than the chain of the substance which they call erucic acid, it is evident that the structure corresponding to figure 4A is the brassidic acid. As is brought out in figure 5, this requires that the ordinary structural formulas for these two acids be interchanged.

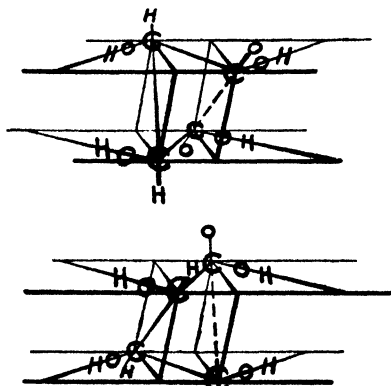


FIG. 7. MOLECULAR STRUCTURE OF DEXTRO- AND LAEVO-TARTARIC ACID (ASTBURY)

According to the latest data (19) available on the saturated hydrocarbons, their chains are like those of the alcohols except that they are stretched in the ratio $\frac{1.3}{1.2}$. The reason for this stretching is not yet clear.

Since almost every elementary text-book in organic chemistry gives so-called stereo-formulas for dextro- and laevo-tartaric acid it will be interesting to see what the real stereo-formulas are. The possible relationships between the atoms permitted by the chemical properties of tartaric acid are shown in figure 6. Astbury's analysis of the crystal structure (20) is shown in figure 7.

The second arrangement in figure 6 is the two-dimensional counterpart of figure 7. It is assumed that the spiral arrangement of carbon atoms is a characteristic of the tartaric acid molecule, but that the spiral arrangement of OH groups is imposed by the crystal. In solution, then, the OH radicals would be free to set themselves at other angles to the carbon atoms, and these new angles need not be rigorously constant, at least in very dilute solutions. All this is consistent with the data to date on the optical activity of tartaric acid.

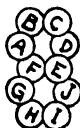


FIG. 8. RING STRUCTURES OF DIAMOND AND GRAPHITE (BRAGG)

THE BENZENE SERIES

The structure of the benzene ring has been a subject for controversy among organic chemists for some time. From the standpoint of x-ray studies, much of this controversy is practically without meaning. W. H. Bragg has pointed out (21) that both diamond and graphite are made up of rings each of which contains six carbon atoms. One such ring alone might be assumed to have the structure of a benzene ring. Two with a common side might represent the carbons in naphthalene, etc. In diamond and graphite, these rings can be studied without the possibility of complications from the atoms of other elements. In figure 8, atoms A B C D E F alone would represent a benzene ring, while A B C D E F G H I J would represent a naphthalene ring. It is seen that the rings resemble hexagons except that they are puckered so that three of the atoms lie on one level and the other three on a parallel but higher level. The difference between this and the ordinary hexagon may be illustrated as follows. Let two equilateral triangles be laid on top of each other in such a way that one is 180° from coincidence with the other. The six corners form a perfect hexagon. Now let one

of the triangles be raised up off the other, but let the planes remain parallel. The six corners now form a puckered hexagon. In naphthalene, the hydrogen atoms attached to A, G, J and D of the ring of figure 8 are called the alpha hydrogens. Those attached to B, C, H and I are called the beta hydrogens.

In terms of Morse's theoretical work (22) and the fragmentary work of Broome (23), Bragg has also proposed a slightly different model of the benzene ring. This need not be discussed here,

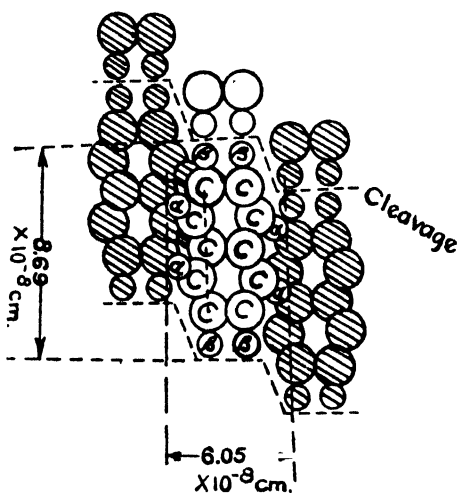


FIG. 9. THREE NAPHTHALENE MOLECULES AND PARTS OF OTHERS (BRAGG)

however, as the new model seems not to have been used in the investigation of crystal structures, and anyway it would make little difference in the end result. The model discussed in this paper is consistent with the work of Dickinson and Bilicke on beta-benzene-hexaldehydes (24). The height* of the puckered hexagon, i.e., the distance from the center of C to the center of E in figure 8, is 2.45×10^{-8} cm. The width is 2.87. In the case of benzene we lack sure experimental data on which to base

* As the structural formula is usually written, this would be the width. The new terminology is employed to make the discussion fit better with the model of the crystal.

any calculations. For naphthalene and anthracene, however, the experimental data are well known (20). Remembering that the "radius" of carbon is to be taken as 0.75×10^{-8} cm., the height of the naphthalene molecule, exclusive of the beta hydrogens is $2(2.45) + 2(0.75) = 6.40 \times 10^{-8}$ cm. The width, exclusive of the alpha hydrogens is $2.87 + 2(0.75) = 4.37 \times 10^{-8}$ cm. The experimental values for the height and width of the naphthalene molecules, including the hydrogen, are 8.69 and 6.05×10^{-8} cm. This leaves $\frac{2.29}{2} = 1.14 \times 10^{-8}$ cm. for the beta hydrogens at each end and $\frac{1.68}{2} = 0.84 \times 10^{-8}$ cm. for the alpha hydrogens on each side. Figure 9 shows that in the

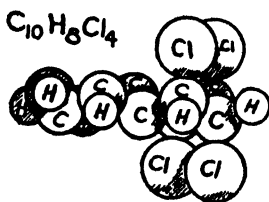


FIG. 10. A MOLECULE OF NAPHTHALENE TETRACHLORIDE (BRAGG)

crystal of naphthalene the alpha hydrogens lie between the carbons of adjacent molecules. They are well crowded, probably by powerful electrostatic forces. The beta hydrogens lie next to the beta hydrogens of adjacent molecules. A repulsive force is to be expected which increases the distance. The measured over-all height includes, of course, half the vacant space at each end of the molecule. For anthracene, the beta hydrogens on each end have 1.16×10^{-8} cm. and the alpha hydrogens on each side have 0.83×10^{-8} cm. These are almost identical with the corresponding spaces allowed for the alpha and beta hydrogens in naphthalene, thus giving additional evidence of the corrections of the stereo-formulas described above.

The new stereo-formulas also receive considerable support from Bragg's investigation of naphthalene tetrachloride (25). The molecule is shown in perspective in figure 10. The increase

in the thickness of the molecule in passing from naphthalene to naphthalene tetrachloride is almost exactly the diameter of two chlorine atoms.

CELLULOSE

X-ray investigations show (25) (26) (27) (28) that cellulose contains orthorhombic crystals each of which is built up of four units of $C_6H_{10}O_5$. This does not mean, however, that the formula for cellulose is $C_{24}H_{40}O_{20}$. For instance, there are three SiO_2 units in an elementary crystal of quartz, but the arrangement of atoms in the crystal makes it very evident that silicon dioxide is composed of elbow-shaped molecules whose formula is SiO_2 . Similarly, in the case of cellulose, the value of n in the formula $(C_6H_{10}O_5)_n$ must be found by a study of the arrangement of atoms in the crystal. Such a study by Sponsler and Dore (28) indicates that n is unity. It is perhaps only fair to say that their work is so far without convincing confirmation.⁴

Further studies (16) show that all cellulose compounds except the diacetate (rayon) are crystalline. It seems, too, that the swelling of cellulose in water consists chiefly in pushing the individual crystals further apart from each other.

There are many other ways in which the x-ray analysis of crystal structure has been of value to the organic chemist. Studies of the packing of organic molecules in crystals not only lead to information of the sort taken up in this paper, but also give a better understanding of many of the physical properties of organic substances. Studies of stretched and unstretched rubber, of gelatin, and of shellac (16) should prove of great importance to the practical chemist. To take up all of these aspects in detail would require a considerable fraction of a book. The writer has therefore limited himself to the narrow field of the stereo-structure of typical organic molecules, in the hope that the contributions of x-ray studies to such a fundamental field will seem important enough to warrant organic chemists in looking up the rest in the literature.

⁴ Note added in reading the proof: In this connection see Houser, Ind. Eng. Chem. 21, 124 (1929).

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THE CHEMISTRY OF ANTHRAQUINONE

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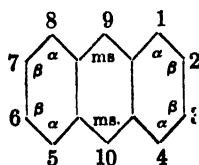
The synthesis of alizarin from anthracene by Graebe and Liebermann (1) in 1868 and the elucidation of the generic relationship between anthracene, anthraquinone, and alizarin by the same investigators, may be said to mark the beginning of a new era in the study of the chemistry of anthraquinone and its derivatives. Although anthraquinone had been prepared by Laurent (2) in 1840 by the oxidation of anthracene with nitric acid and subsequently by Fritzsche (3) by the oxidation of anthracene with chromic acid, little interest was attached to this compound until Graebe and Liebermann announced their epoch-making discovery. This soon led to the technical production of synthetic alizarin (4) and stimulated research to such a marked degree that today we may with propriety speak of an "anthraquinone chemistry." In this paper a review will be presented of the more important facts pertaining to the chemistry of this compound.

CONSTITUTION AND NOMENCLATURE

Constitution. The quinone-like character of anthraquinone was first clearly recognized by Graebe and Liebermann (5), who showed that it bore the same structural relationship to anthracene as benzoquinone did to benzene. The name "anthraquinone" was first proposed by these two investigators (5). The generally accepted diketo formula for this compound was suggested by Fittig (6). The synthesis of anthraquinone from benzoyl-2-benzoic acid, which will be discussed elsewhere in this paper, is a further proof of its structure.

Nomenclature. The generally accepted system of nomencla-

ture is the following. The ten positions in anthracene are numbered as indicated below.



Positions 1, 4, 5 and 8 are frequently referred to as the α positions; and positions 2, 3, 6 and 7, as the β . The 9 and 10 positions are sometimes designated as the meso- or ms-. Of the six theoretically possible monoquinones of anthracene, namely, 1,2; 2,3; 1,4; 1,5; 2,6; and 9,10, the last one only is of any practical importance. When speaking of "anthraquinone" the 9,10 anthraquinone is generally understood.

PREPARATION

From anthracene. The anthracene fraction of "anthracene oil" (280° to 400°C.), obtained in the distillation of coal tar, is allowed to stand, and the crystals which separate out, consisting of anthracene, carbazol, phenanthrene, etc., are subjected to hot pressing and then to purification by washing either with solvent naphtha or pyridine. This process gives a product containing about 50 per cent anthracene. This mixture is distilled in a current of superheated steam, and the vapor condensed by means of fine jets of water, thus reducing the anthracene to a state fine enough for oxidation. The distillate is then oxidized with the calculated amount of sodium dichromate and sulfuric acid, thereby converting the anthracene to anthraquinone without greatly affecting the impurities. In order to free the anthraquinone from these impurities, use is made of a method first proposed by Luck (7), which consists in treating the oxidation product with two to three parts of concentrated sulfuric acid of 66° Bé and heating the mixture at 110°C. This treatment sulfonates the impurities, but not the anthraquinone. The hot sulfonation mass is poured into boiling water, and the anthraquinone is precipitated out in a form suitable for filtration.

The filtrate contains the impurities. The anthraquinone thus obtained is usually further purified by sublimation.

SYNTHETIC

From benzoic acid. When benzoic acid is heated with a suitable dehydrating agent, such as phosphorus pentoxide, anthraquinone is obtained (8). When an hydroxy benzoic acid is used, the condensation proceeds more easily and hydroxy anthraquinones (9) are formed.

From phthalic anhydride directly. This method which is useful in the preparation only of derivatives of anthraquinone, especially hydroxy-anthraquinones, consists in heating phthalic anhydride and a phenol or a phenol derivative with concentrated sulfuric acid and boric acid. Thus p-chlorophenol and phthalic anhydride yield quinizarin (10). Anthraquinone itself can not be prepared by this method.

From phthalic anhydride, benzene, and anhydrous aluminum chloride. This is the only method technically used in the preparation of synthetic anthraquinone. Phthalic anhydride is first condensed with benzene and aluminum chloride to give benzoyl-2-benzoic acid, which when heated with sulfuric acid is converted into anthraquinone. In view of the tremendous technical importance of this method, an historical review of its development may be in place here.

Anthraquinone was first prepared synthetically from o-benzoyl-benzoic acid by Behr and van Dorp (11). By heating one part of o-benzoyl-benzoic acid with two parts of P_2O_5 at $200^\circ C$. for several hours, these investigators succeeded in obtaining a 26 per cent yield of anthraquinone.

Liebermann (12) in attempting to improve on the foregoing method substituted fuming sulfuric acid in place of the P_2O_5 and found that this acid acted as a sulfonating agent as well as a condensing agent. The final product obtained was anthraquinone sulfonic acid, which he was able to convert into alizarin.

The fundamental scientific work of the present synthetic anthraquinone process was done by Friedel and Crafts (13). In applying their reaction, now well-known, to phthalic acid chloride

and benzene, they obtained a reaction product consisting of two substances, namely, phthalophenone and anthraquinone. They assumed that in this reaction the benzene and anhydrous aluminum chloride reacted first to give an intermediate compound represented by the formula $C_6H_6 \cdot Al_2Cl_6$ and that this compound then reacted with the phthalic acid chloride to give phthalophenone and anthraquinone (14).

Studying this fundamental reaction further, these investigators reported in the following year (1878) that when phthalic anhydride was used in place of the phthalic acid chloride, the principal reaction product was o-benzoyl-benzoic acid (15). No information regarding yield obtained or procedure followed in carrying out the reaction is given.

In 1880, v. Pechmann (16) prepared o-benzoyl-benzoic acid by the method of Friedel and Crafts and reported a yield of 60 per cent of the weight of phthalic anhydride used (41 per cent of theory). A small amount of diphenylphthalide (17) was also formed in this reaction.

In 1891 Perkin (18) showed that when o-benzoyl-benzoic acid is heated at $100^\circ C.$ with concentrated sulfuric acid instead of the fuming sulfuric acid used by Liebermann (12), a quantitative yield of anthraquinone is obtained.

Haller and Guyot (19) in a paper published in 1894 reported that they succeeded in obtaining a 92 per cent yield of o-benzoyl-benzoic acid, using the method of Friedel and Crafts. They failed, however, to give any details concerning the manner in which this reaction was carried out.

Graebe and Ullmann (20) give the following directions for the preparation of o-benzoyl-benzoic acid: Fifty grams phthalic anhydride (1 mole) is dissolved in 250 cc. benzene, and 70 to 75 grams (0.82 mole) finely powdered Al_2Cl_6 is added. This mixture is heated on the water bath until no more HCl is evolved (two hours). The reaction product is decomposed with water and steam distilled to remove the unused benzene, and the residue is digested with Na_2CO_3 solution. The yield amounts only to 85 per cent of the theory, owing to the fact that an insufficient amount of aluminum chloride is used.

Heller (21) was the first to make a systematic study of the reactions involved in the preparation of synthetic anthraquinone from phthalic anhydride, anhydrous aluminum chloride, and benzene. He showed conclusively (1906) that the aluminum chloride does *not* act catalytically but forms an intermediate compound with the phthalic anhydride and benzene. To get the best yield of o-benzoyl-benzoic acid, one mole of Al_2Cl_6 must be added for every mole of phthalic anhydride used. His directions for obtaining the best yield of anthraquinone are as follows:

To 1 kgm. (1 mole) of phthalic anhydride and 3.5 kgm. benzene (6.6 moles), contained in a lead-lined vessel, 1.8 kgm. (1 mole) Al_2Cl_6 is added all at once. The reaction mixture is heated gradually to 70°C . and maintained at this temperature until no more HCl is evolved. Water is added to the reaction mixture, the excess benzene is distilled off, the residue is digested with Na_2CO_3 solution and filtered, and the filtrate is acidified. The yield of o-benzoyl-benzoic acid is 95 to 97 per cent of theory. This acid is converted into anthraquinone by heating it with 5 to 6 parts of sulfuric acid (66°Bé) at 150°C . The yield is quantitative.

In 1908 Heller and Schulke (22) studied the mechanism of the reaction involved in the synthesis of o-benzoyl acid and concluded that the reaction first produces an addition compound having the composition represented by the formula $\text{C}_8\text{H}_6\text{O}_3 \cdot \text{Al}_2\text{Cl}_6 \cdot \text{C}_6\text{H}_6$. This product then decomposes with the elimination of HCl , giving the second intermediate compound $\text{C}_{14}\text{H}_6\text{O}_3 \cdot \text{Al}_2\text{Cl}_6$, which then treated with water forms the aluminum salt of o-benzoyl-benzoic acid.

Rubridge and Qua (23) confirmed Heller's findings with regard to the part played by the aluminum chloride in this reaction. When less than one mole of Al_2Cl_6 was used for each mole of phthalic anhydride, diphenyl phthalide was formed, a result which was found to be due to the action of the excess of phthalic anhydride on the intermediate compound.

Harding (24) carried out the preparation of synthetic anthraquinone on a semiindustrial scale. The process as described by him is essentially the one now used commercially. It will be

noted that it is similar to the method recommended by Heller (21).

One and eight-tenths (1.8) parts Al_2Cl_6 and 1 part benzene by volume are put into the reaction kettle, which is lead-lined, jacketed for cooling, and provided with a good stirrer and reflux condenser. It is connected to a scrubber system for the absorption of the HCl generated. One part of phthalic anhydride is dissolved in 4 parts benzene, and this solution is run into the reaction kettle by means of a jacketed pipe. The temperature is gradually raised to 35°C . and the reaction begins, with the evolution of HCl . This temperature is maintained for twenty to thirty minutes, then slowly increased to 75 to 80°C . within an

TABLE 1
Anthraquinone produced in the United States, 1919-1924

YEAR	POUNDS
1919	294,260
1920	539,619
1921	125,358
1922	395,107
1923	857,910 (about 50 per cent synthetic)
1924	638,755 (about 75 per cent synthetic)

hour, and maintained at this temperature until no more HCl is evolved. The excess benzene is distilled off under reduced pressure. The dry residue, which is easily powdered, is decomposed either with hot water or with hot Na_2CO_3 solution. The yield of o-benzoyl-benzoic acid is about 95 per cent of theory or 145 per cent of the weight of the phthalic anhydride used.

For the conversion of the o-benzoyl-benzoic acid into anthraquinone, 1 part of the anhydrous acid is heated with 4 parts 95 per cent H_2SO_4 at 130°C . for from three-quarters to one hour with good stirring. An ordinary sulfonator is suitable for this condensation. The sulfuric acid solution of the anthraquinone is poured into water, cooled and centrifuged. This anthraquinone is further purified by sublimation with steam. The overall yield

of sublimed anthraquinone on the phthalic anhydride used is more than 120 per cent by weight (85 per cent of theory).

Table 1 gives the quantity of anthraquinone produced in the United States during the period 1919–1924. These figures are taken from the annual reports issued by the United States Tariff Commission ("Census of Dyes and Other Synthetic Organic Chemicals," United States Tariff Commission, Washington, D. C.).

It is understood that a considerable quantity of anthraquinone was produced during the years 1925 and 1926, but the Tariff Commission could not publish these figures without disclosing the operation of individual firms.

Sulfonation. Anthraquinone does not sulfonate easily with ordinary concentrated sulfuric acid, and fuming sulfuric acid is therefore generally employed. This leads to the formation of the β acid together with a small amount of disulfonic acids, principally the 2,6 and 2,7 acids (25). In the technical production of the β acid an excess of anthraquinone is used, and the formation of the disulfonic acids is then reduced to the minimum. The sulfonation mass is poured into water, the excess anthraquinone is filtered off, and the filtrate is neutralized with sodium carbonate. The rather insoluble sodium salt of anthraquinone-2-sulfonic acid then separates out. Because of its silver-like appearance this salt is technically known as "silver salt."

Until 1903, it was generally held that the anthraquinone- α -sulfonic acid could not be obtained by direct sulfonation of anthraquinone. It was found, however, by Schmidt (26), and also by Iljinsky (27), that if a small amount of mercuric sulfate is added to the sulfonation mixture the α acid is obtained almost entirely (28). On further sulfonation the 1,5 and 1,8 disulfonic acids are produced together with a small amount of trisulfonic acid (29).

As a rule, the anthraquinone sulfonic acids are fairly easily desulfonated by hydrolysis, although the ease with which the sulfonic group is eliminated varies to a great extent in different substances. Ordinarily, the sulfonic acid group in the α position is more easily removed than one in the β position (30). It will be

recalled that the monosulfonic acids of naphthalene behave similarly.

Nitration. When anthraquinone is nitrated the α position is first substituted. No β nitroanthraquinone is formed in this reaction. The nitration is carried out by dissolving the anthraquinone in concentrated sulfuric acid and adding concentrated nitric acid to this solution (31). The β nitroanthraquinone can not be prepared by direct nitration and is generally made by nitrating β aminoanthraquinone and then removing the amino group from the resulting 2-amino-3-nitroanthraquinone by the diazo reaction (32).

Halogenation. Anthraquinone is attacked by halogens only with the greatest difficulty, although the classical synthesis of alizarin from anthraquinone by Graebe and Liebermann was brought about by brominating the anthraquinone in a sealed tube at 100°C. and fusing the resultant dibromo derivative with alkali. A more simple method, however, is first to brominate anthracene and then to oxidize this to the corresponding bromo derivative of anthraquinone (33). In general, the halogen derivatives of anthraquinone are obtained by indirect methods, that is, by replacing a substituent already present in the anthraquinone molecule. Thus chloroanthraquinone can be prepared from aminoanthraquinone by the diazo reaction or by the treatment of an hydroxy anthraquinone with phosphorus pentachloride, phosphorus oxychloride, or phosphorus trichloride (34).

Halogen anthraquinones may be readily prepared from the corresponding sulfonic acids. Sulfonic acid groups either in the α or β positions are readily replaced by chlorine or bromine. Thus α -chloroanthraquinone may be obtained in excellent yield by adding sodium or potassium chlorate to an acid solution of anthraquinone α -sulfonic acid. The nascent chlorine liberated in this reaction replaces the sulfonic acid group (35).

Another satisfactory method for preparing halogen derivatives of anthraquinone is the phthalic anhydride synthesis. Thus, if monochlorobenzene is condensed with phthalic anhydride and aluminum chloride, chloro-benzoyl-benzoic acid is obtained, which

on condensation with concentrated sulfuric acid is converted into 2-chloroanthraquinone (36). By starting with p-dichlorobenzene 1,4-dichloroanthraquinone is obtained (37). If o-dichlorobenzene is condensed with phthalic anhydride, however, the principal product of the reaction is 2,3-dichloroanthraquinone, together with a small amount of 1,2-dichloroanthraquinone (38). In a similar manner halogen derivatives of anthraquinone may be obtained by condensing chlorophthalic acids with benzene and aluminum chloride (39).

Amidation. The amino anthraquinones are of great commercial importance, being used as intermediates in the preparation of a number of important anthraquinone dyes. They are generally prepared either by the reduction of the corresponding nitroanthraquinone or by the replacement of negative substituent groups in the anthraquinone molecule, such as halogen atoms, hydroxyl, or sulfonic acid groups.

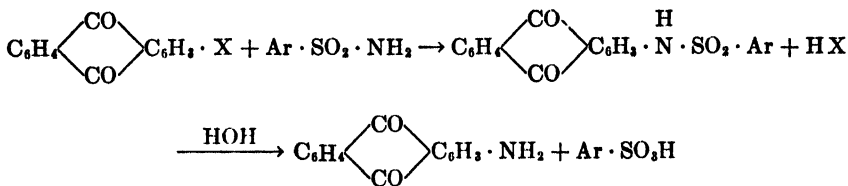
The most satisfactory reagent for the reduction of the nitroanthraquinones is sodium sulfide, and, as a rule, the yields obtained by this method are very good (40). The reduction may also be brought about with tin and hydrochloric acid (41), sodium stannite, zinc dust, and sodium hydroxide or ammonia (42).

REPLACEMENT OF NEGATIVE GROUPS

Replacement of halogen atoms. When heated with aqueous ammonia under pressure halogen anthraquinones are converted into the corresponding amino derivatives. Thus, when heated with aqueous ammonia in an autoclave, 2-chloroanthraquinone is converted into 2-aminoanthraquinone (43). If, in place of ammonia, an alkyl or aryl amine is used, the corresponding secondary aminoanthraquinone is formed (44).

The reaction between ammonia or alkyl amines and halogen anthraquinones will generally take place only when the substances are heated together in an autoclave under pressure. Ullmann (45) in 1910 discovered that sulfonamides will condense with halogen anthraquinones at ordinary pressure. On hydrolysis the condensation product gives the aminoanthraquinone.

This reaction may be represented as follows:



The sulfonamide generally employed in this reaction is p-toluene sulfonamide, a by-product in the manufacture of saccharin. If in place of p-toluene sulfonamide an N-alkyl or N-aryl substitution product is used in this reaction, the corresponding secondary aminoanthraquinone is obtained.

Replacement of hydroxyl groups. The hydroxyl group can generally be replaced by an amino group by heating the hydroxy compound with ammonia or with an alkyl or aryl amine (46). This reaction is made use of in the preparation of a number of dyes, such as Quinizarin Green; Alizarin Irisol; Alizarin Direct Green G, and Alizarin Brilliant Green G. The condensation is brought about by first reducing the hydroxy anthraquinone to the leuco compound, then condensing with the aromatic amine in the presence of boric acid, and finally oxidizing this product to the amino anthraquinone derivative (47).

Replacement of sulfonic acid groups. Another important method of preparing aminoanthraquinones is by replacing the sulfonic acid groups. Thus, 2-aminoanthraquinone, which is extensively used in the preparation of anthraquinone vat colors, is obtained from sodium anthraquinone-2-sulfonate ("silver salt" of commerce) by heating it with aqueous ammonia in an autoclave under pressure. In order to obtain the best yields of 2-aminoanthraquinone it is necessary to destroy the sodium sulfite formed as a by-product in this reaction. This is usually done either by the addition of barium chloride (48), which reacts to form the insoluble barium sulfite, or by the addition of manganese dioxide (49), which oxidizes the sulfite to the inactive sulfate.

The aminoanthraquinones may be alkylated or arylated in the

usual manner by heating the amino compound with alkyl or aryl halide. The arylation, however, is preferably conducted in the presence of a copper catalyst and sodium acetate or potassium carbonate (50).

HYDROXYLATION

The hydroxyanthraquinones are of considerable technical importance; like alizarin they are used as dyes and as intermediates in the preparation of other anthraquinone derivatives. They are phenolic in character giving soluble phenolates with the fixed alkalies. These soluble phenolates form "lakes" with iron, tin, antimony, and aluminum. The hydroxyl group in any position can be readily acylated, but an hydroxyl in the α position can not be alkylated.

There are four general methods for introducing an hydroxyl group into the anthraquinone nucleus. They are:

- (1) Replacement of a sulfonic acid group.
- (2) Replacement of an halogen atom.
- (3) Replacement of an amino group.
- (4) Direct oxidation.

The replacement of a sulfonic acid group by fusion with caustic alkali is an important method and is used commercially for the production of alizarin from sodium anthraquinone-2-sulfonate. The alkali fusion of this sulfonate proceeds abnormally, in that during the alkali melt simultaneous oxidation takes place, and usually the number of hydroxyl groups in the product is greater than the number of sulfonic acid groups in the original sulfonic acid. In the alkali fusion of sodium anthraquinone-2-sulfonate, hydrogen is liberated, reducing a part of the alizarin to monohydroxyanthraquinone or even to anthraquinone itself. This used to occur in the early days of the manufacture of synthetic alizarin, but is now obviated by adding sodium chlorate or nitrate to the melt, an improvement introduced by Koch (51). When the sulfonic acid group is in the α position, fusion with alkali usually leads to the rupture of the benzene ring. Sulfonic acid groups in any position in the anthraquinone molecule,

however, can be replaced by hydroxyl groups (without simultaneous oxidation taking place as in alkali fusion) by heating the sulfonic derivative with an aqueous solution of calcium or barium hydroxides at a temperate of 150 to 180°C. (52).

Replacement of halogen atoms. When attached to the anthraquinone nucleus halogen atoms may be replaced with hydroxyl groups by the fusion with alkali. Thus Graebe and Liebermann effected the first synthesis of alizarin by the fusion of dibromoanthraquinone with potassium hydroxide. The reaction, however, proceeds abnormally, in that an intramolecular migration takes place. For example, by the alkali fusion of 2,3-dichloroanthraquinone, the chief product of the reaction is alizarin and not hystazarin (53).

Replacement of amino groups. Amino groups can be replaced with hydroxyl groups in the usual manner, through the diazo reaction. As a rule, it is best to diazotize the amino compound in concentrated sulfuric acid, and then break off the diazo group by heating to 90° to 100°C. (54). This method of introducing hydroxyl groups is, however, of no great technical importance.

Direct oxidation. Anthraquinone differs from the aromatic compounds in the great ease with which hydroxyl groups can be introduced into the anthraquinone molecule. The simultaneous oxidation of anthraquinone-2-sulfonic acid to alizarin by fusion with alkali has already been referred to. Another reaction used in the introduction of hydroxyl groups into the anthraquinone nucleus is what is known as the Bohn-Schmidt reaction (55). This reaction consists in introducing hydroxyl groups into the anthraquinone molecule by the oxidizing action of fuming sulfuric acid. Subsequently Schmidt (56) discovered that if boric acid is added to the reaction mixture, ordinary concentrated sulfuric acid may be used in place of the oleum. The boric acid forms esters with the hydroxyanthraquinones and prevents the oxidation from going too far. The importance of this reaction can be appreciated from the fact that it is used in the technical preparation of such important dyes as Alizarin Green S, Alizarin Bordeaux, Alizarin Cyanine R, and Alizarin Cyanin Black.

OXIDATION AND REDUCTION

Anthraquinone is stable to oxidizing agents. If too severe oxidation is resorted to, complete disruption of the molecule takes place. Alkyl side chains when present may, however, be readily oxidized with nitric acid (57) to the corresponding carboxylic acids.

Reduction. Unlike benzoquinone, anthraquinone can not be reduced with sulfurous acid. Tin and hydrochloric acid reduces it to anthranol (58). It can be reduced with several alkaline reducing agents, such as zinc dust and ammonia, and glucose and alkali, but the most important reducing agent is "sodium hydrosulfite" (hyposulfite). On reduction with "hydrosulfite" the carbonyl groups are reduced to hydroxyl groups, or anthranols. These anthranols are alkali-soluble and are reoxidized to the corresponding anthraquinone by atmospheric oxygen. This property of undergoing reversible oxidation and reduction makes it possible to use many of the anthraquinone derivatives as vat dyes.

HOMOLOGUES

The alkyl anthraquinones are generally prepared via the phthalic anhydride synthesis. Thus from toluene, phthalic anhydride and aluminum chloride, 2-methyl anthraquinone is obtained (59). From the xylenes, the corresponding dimethyl anthraquinones are obtained (57). *p*-Cymene yields 1,4-methyl isopropyl anthraquinone (60). With the exception of 2-methyl anthraquinone, the alkyl anthraquinones are of no technical importance.

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PRESENT STATUS OF THE MOLECULAR FIELD PROBLEM¹

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INTRODUCTION

When certain general principles began slowly to emerge from the mass of chemical facts available some fifty years ago, it was the classical theory of energy transformations which quite naturally proved the most useful tool for purposes of correlation and giving precision to the developing ideas. Indeed, thermodynamics is a branch of Physics peculiarly suited for the discussion of the complex interplay of the different manifestations of energy change to be found associated with chemical processes.

While thermodynamics proved sufficient for correlating almost the entire range of experimental facts which were formerly considered by the student of chemistry, in our day a wide variety of phenomena has accumulated to a wholly amazing degree. In fact, the theory of the properties of solutions in all states of aggregation, the interpretation of chemical equilibria, and the transformation of chemical energy into electricity included, scarcely twenty years ago, almost the entire range of the subject of physical chemistry. The progress of the experimentalists' art has, however, brought forward a large mass of facts concerning adsorption, catalysis, the colloidal state, rates of reaction, the action of light energy in relation to chemical change, surface tension and spectral characteristics as related to molecular structure, for the understanding of which thermodynamical treatment alone does not go far enough. It is the kinetic theory in an extended form, which promises to provide the most convenient basis for ordering and interrelating these phenomena.

¹ Contribution from the Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology, No. 217.

The kinetic theory of matter has always been, more or less, a subject of serious study by the chemist, but in the period of the development of the earlier physical chemistry the comprehensive and beautiful correlation of chemical facts with the aid of thermodynamics inclined many to the opinion that at least for a very long time, the kinetic theory was to play the rôle of an interesting but somewhat minor adjunct in the development of the science. It is true there were, and still remain, many serious theoretical difficulties to be surmounted in the kinetic theory, in contrast to thermodynamical theory, which, keeping aloof from mechanical hypotheses, is based on absolutely general principles. Nevertheless, the developments of the quantum theory have gone far to remove some of the theoretical difficulties hampering the classical kinetic theory, notably those connected with specific heats, and the recent investigations in "quantum statistics" promises important developments which may soon place the general theory on an entirely satisfactory theoretical basis.

It may be apropos to refer briefly to the nature of some of the more important difficulties which have beset the classical (Newtonian) statistical mechanics. The heat capacities of the monatomic gases appear to have the value predicted by the classical theory, namely $3R/2$. To obtain the latter value, however, it is necessary to neglect the energy of rotation and assume that the molecule possesses no energy other than translatory. Monatomic atoms (or monatomic molecules) are known to possess, however, an extremely complicated internal structure as evidenced, for example, by their spectra; and the question arises as to how the internal energy of the atom can be so completely independent of the energy of translation. Stating the matter in a somewhat different way: how is it that the energy of translation is not lost to the internal vibratory energy of the atoms with an attendant continual diminution of the translatory energy? No satisfactory answer to this problem can be given by a kinetic theory based on Newtonian mechanics. Thus, helium is known to consist of a positive nucleus and two electrons. This should give, counting each component of the translatory energy as contributing $R/2$ calories to the specific heat, a heat capacity of $3R/2$ for the trans-

lational energy plus, possibly, $3R/2$ for each particle constituting the atom or $12R/2$ calories as the maximum conceivable heat capacity.

These difficulties in the kinetic theory and others related thereto were known to Maxwell and referred to by Lord Kelvin in his Baltimore lectures as a cloud over the kinetic theory. The quantum theory has done much to clear away the cloud although not with final completeness.

The general quantum theory answer to the difficulty is that there is a lack of analogy between the internal vibratory processes going on within the atom and the translatory motions of the atoms as a whole. The mechanism governing the transfer of energy due to the motion of the electrons constituting the atom (the interatomic and intramolecular energy) to space is controlled by the operation of special laws (quantum dynamical laws) differing completely from the Newtonian dynamical laws, which have been assumed to govern the translatory energy.

The development of these newer dynamical laws has not, however, stopped with their application to the movement of the particles constituting the atom, but considerations of a quantum nature applied to the translatory energy lead to a modification of the deductions relative to a monatomic gas at very low temperatures. The latter problem is still in a state of flux; Einstein and Bose, for example, proposing a form of statistics leading to a perfect gas expression where pressures are predicted to be less than those given by $p = RT/v$ while Fermi-Dirac basing their statistics on the Pauli (1) "dictum" predict a precisely opposite effect.

The situation presented then is briefly that the expanding range of phenomena of special interest to the chemist requires as a medium for discussion and correlation a kinetic theory firmly grounded on a broadened or rather generalized statistics. Richard C. Tolman has well emphasized this in a recent excellent book (2) where an introduction of quantum ideas into the classical mechanics is attempted, rather than the more radical step of Dirac where about the only portion of the older ideas retained is that entropy is assumed proportional to probability; a proba-

bility however redefined to incorporate a generalization of the Pauli dictum.

If the chemist were interested alone in the validity of the "perfect gas" equation, he would have little to be concerned about. There is, however, considerably more than this involved in the problems which must be solved in connection with photo-chemical effects, reaction velocities, colloid behavior, the equation of state problem, referring to but a few of the types of phenomena which are of fundamental importance in the science. The main object of the present paper is to call to attention and to discuss in some detail several properties of matter, an accurate experimental knowledge of which would aid substantially in arriving at a decision as to the value of some of the speculative ideas being applied in treating theoretically the various classes of phenomena referred to above. As already suggested the important general problem of particular interest to the physical chemist is that concerned with the development of a kinetic theory having as a basis *generalized* statistics which will avoid the difficulties which have surrounded the classical statistics.

THE MOLECULAR FIELD

The classical kinetic theory was found to suffice to a considerable extent in explaining the range of experimental facts available up to perhaps 75 years ago. It is true that Joule and Thomson's porous plug experiment had indicated that a molecular model of the perfectly reflecting type characterized by mass and velocity, was insufficient to explain the effect obtained with nitrogen and carbon-dioxide or the opposite sign of the effect in the case of hydrogen. Moreover, Regnault's and Andrews' experimental results as well as those of others, made it abundantly clear that the simplicity of the laws of gases was at best a condition which obtains for a gas only at very low pressures. The notion of endowing the classical model with an attractive field had been proposed at various times by various people (3) but no one did anything very seriously about the matter, at any rate in the case of gases, until van der Waals' attempt was presented in the 1873 Essay. Hirn (4) had pointed out some years before van der

Waals' essay appeared that a "cohesive pressure" might aid in explaining the failure of the gas laws (Boyle, Gay-Lussac).

The van der Waals' model consists then of the classical molecular model with the addition of an attractive field of spherical symmetry. The carrying out of the computation of the equation of state by van der Waals for what may be called a "van der Waals' model" was not in all details satisfactory. In fact, it is easy to show that the final equation of van der Waals is accurate only at high temperatures and low pressures for a gas composed of molecules of the van der Waals' type. The principles involved in the general computation are of such importance and interest, and are so often omitted in books treating of physical chemistry, that certain important considerations relative to the van der Waals' model and its treatment will be reviewed.

We may begin by remarking that a molecule whose molecular field is solely attractive seems artificial in view of the need of also imagining a repulsive field to "balance the attraction" (5). The difficulty may be much relieved by considering further the specification of the assumed perfectly-elastic quality of the model. In interaction, or collision, a pair of classical or van der Waals' molecules of diameter d are assumed to develop mutually a large (infinite) repulsive force for distances of separation less than d (the distance between centers) and a force precisely zero for distances in excess of d . The repulsive action may be assumed therefore to take place over an infinitely thin spherical shell surrounding the molecule. Such conditions of interaction would follow if the repulsive force R is put, for example, equal to $\lambda_n r^{-n}$, and n becomes mathematically infinite. Otherwise expressed the van der Waals' model may be viewed as one possessing a repulsive field, the index of which, n , is very large or infinite. The condition of infinite n need not be taken in the literal sense for it will be shown later that $n = 15$ is a practical approximation for mathematical infinity in accounting for the physical properties of certain gases. Assuming the above considerations to remove the difficulty presented by the apparent absence of a repulsive field for a van der Waals' model, the nature and mode of action of the attractive field remains to be considered.

The attractive field for simplicity, may be represented analogously to the repulsive field by $\pi_m = f(r^{-m})$. Many have assumed that π_m was simply $\lambda_m r^{-m}$ where λ_m is a constant,² m ranging from 2 to several times the latter number. Calling into consideration the information now available concerning atomic structure this simplicity seems scarcely acceptable. Leaving this detail aside for the present, however, it will be assumed that π_m is given by $\lambda_m r^{-m}$ and certain limitations of van der Waals' original deduction of the cohesion pressure may be mentioned.

As long as molecular fields are assumed absent the classical theory states that the distribution of the molecules within a given range of velocities will be determined solely by the kinetic energy of motion of the molecules. The presence of either an attractive field or repulsive field, or both, introduces another factor, for it is easily perceived that the probability of "nearness" of two neighboring molecules will be greater in an attractive field and less in a repulsive field. In fact, the probability of a number of molecules possessing a given range in the velocity space, $dx dy dz$, is proportional (classically) to the expression $e^{-\frac{\epsilon}{kT}}$ where ϵ is the kinetic energy of a molecule, k being Boltzmann's constant and T the absolute temperature. Similarly, if $\int \pi_n dr = \varphi_n$ and $\int \pi_m dr = -\varphi_m$ are the potential energies of repulsion and attraction respectively, the "probabilities of position" may be taken proportional to $e^{-\frac{\varphi_n}{kT}}$ and $e^{+\frac{\varphi_m}{kT}}$. There entering no other types of energy into the consideration, the number of molecules to be found in any part of the generalized gas space (positions at the walls of the containing vessel being excluded) is proportional to the product of the separate probabilities

$$e^{-\frac{(\epsilon + \varphi_n - \varphi_m)}{kT}}$$

It is now clear from this expression that there will be a tendency, due to the attractive field, for the molecules to cluster or

² The notation has been adapted from the paper of J. E. Jones (6).

aggregate, also this latter tendency is opposed by the repulsive field (disaggregation) and increasing kinetic energy. The aggregation tendency, in short, is opposed by the repulsive property and increase of temperature.³

van der Waals proceeded differently. He took as a consequence of the assumed finite and invariable molecular diameter, a free path shortening leading, by a not quite valid computation, to $p = \frac{RT}{v - b}$ for the pressure, where b is the fourfold molecular volume. To the latter equation, van der Waals then merely added

$-\frac{a}{v^2}$ as a result of general considerations leading from La Place's capillarity theory.⁴ Thus, the aggregation effect is not included and since the latter effect is effaced at high temperatures it is evident that van der Waals' deduction may be regarded as possessing greatest validity if applied to a gas at high temperatures (strictly T infinite) and low pressures. The form of the resulting equation happens to be such as to reproduce in a qualitative way the isotherms of a gas-liquid system. The equation has therefore been used to discuss the liquid state which is not strictly legitimate as indicated by the theoretical status of the equation. Indeed the aggregation effect is to be regarded as *one* of the principal factors in bringing about the existence of the liquid phase; an effect as already shown, not included in the van der Waals' equation.⁵

Besides van der Waals' treatment of the molecular field in

³ It is to be noted that kT in the probability exponential is equivalent to θ in Gibb's statistical treatment. Gibbs does not make the identification between $\frac{\theta}{k}$ and temperature, contenting himself, at most, by implying that θ is analogous to temperature in the case of a gas.

⁴ The use made by van der Waals of La Place's theory may well raise objections since the latter theory is based on the conception of an incompressible fluid and the effect of molecular movement is ignored. In fact the theory even ignores altogether the existence of molecules.

⁵ It may indeed be found that the classical mechanics are insufficient to provide the proper basis for discussing quantitatively the conditions insuring the existence of the liquid phase.

the case of the equation of state problem, many (7) (8) (9) (10) (11) (12) (13) (14) (15) have given more exact computations, not alone for the van der Waals' model but for other simple models.

THE ORIGIN OF THE MOLECULAR FIELD

Thus far the existence of a molecular field, attractive or repulsive, symmetrically disposed about the molecular model, has been merely postulated. The origin of such fields is a matter of the greatest importance if further progress in the kinetic theory from the quantitative point of view is to follow. We owe Debye's (16) (17) fertile imagination an explanation, consistent with modern views regarding atomic structure, of the origin of these fields. It is true that the information regarding the structure of atoms and molecules is altogether insufficient at present to permit of the desired quantitative development of Debye's ideas, but it is already clear that these ideas are correct and will serve to guide properly conceived investigations into a path leading in time to a satisfactory understanding of the molecular field. The matter is of so much importance and has been referred to so meagerly in the physico-chemical literature that a brief sketch of Debye's ideas may be apropos in the present paper.

Considering atoms or molecules in any state of aggregation, it is a familiar fact that the dielectric constant and refractive index is greater than for a vacuum. To account for these phenomena it was long ago assumed by Sellmeyer and Helmholtz, for example, that the atoms or molecules possessed charged particles (electrons) bound into positions within the molecule by means of elastic forces: the distance of displacement of the electrons under the action of light or any electric field being assumed proportional to the displacing force acting. Such a simple basis was fruitful in leading to the Lorenz-Lorentz equation $\frac{n^2 - 1}{n^2 + 2} \frac{1}{\rho} = \text{constant}$ where n is the refractive index and ρ the density. The same atomic model suffices to give the Clausius-Mosotti equation $\frac{D - 1}{D + 2} \frac{1}{\rho} = \text{constant}$, where D is the dielectric constant. To

assume, therefore, that the electrons composing the atom are immovable under the action of the electric light vector or the electric field amounts to denying the possibility of the refractive index or dielectric constant being different from that of a vacuum. The displacement of the electric charges, or the *equivalent* of a displacement, may accordingly be accepted.

Now a collection of molecules constituted of a positive portion and electrons sufficient in the aggregate of their negative charge to neutralize the positive charge, will exert a mutual electrical influence upon one another. For example, consider the center of electrical effect for the positive electricity to coincide with the electrical center for the negative electricity in a single molecule removed from the action of every similarly constituted molecule or electrical effect. Now bring this molecule whose constituting charges are movable into the presence of one or more similar molecules. The reciprocal effect of the molecules one upon the other (regardless of orientation or kinetic energy) will be to separate the centers of electrical action of the positive and negative charges in each molecule from coincidence, producing thereby an *induced* polarity. The induced polarity may be regarded in every way as similar to that produced by the action of an outside electrical field in the case of the dielectric property or the electric vector of light in the case of the refractivity. Let the induced electrical polarization of the molecule be α and the electric field arising from the electric charges constituting the molecule and inducing the moment be represented by E . Then the electric moment is αE . The work necessary to bring a molecule from a point where the field E_1 is zero into the midst of the gas where the field is E will be $-\alpha E \frac{E}{2}$ or $-\frac{\alpha E^2}{2}$. The quantity α , the induced polarization is therefore proportional to the constant of the Clausius-Mosotti formula, namely $\frac{D-1}{D+2} V = \text{Constant} = \frac{4}{3} \pi N \alpha$. A computation of the average squared electric field $\overline{E^2}$ in terms of the number and positions

of the electric particles composing the atoms will in principle lead directly to an expression for the potential energy between any two molecules or ϕ_m referred to above. $\left(-\frac{3}{r^3} \alpha \tau^2 \right)$ for quadrupole⁶ molecules where τ is the electrical "moment of inertia," i.e., charge \times (distance)², and r is the distance between the centers of the molecules.)

The origin of the repulsive field is not quite so easily understood. To illustrate the thought, assume that the electrons move in orbits about a central positive charge as is visualized in the Bohr atomic model (the "reality" of the original Bohr orbits is, on the newer quantum theory, no longer as definitely conceivable). The nature of the effect accounting for the repulsive force may be made definite by considering the example selected by Debye; a Bohr hydrogen atom represented by a positive

⁶ The terms dipole, quadrupole, octapole, etc., are designations which may be applied to molecules when definite positions are assigned to the positive and negative charges of which the molecule (or atom) is assumed to be composed. Thus a Bohr model of the hydrogen atom assumes an electron to be rotating in orbital motion about a positive charge whose magnitude is equal to that of the electron. Such a model may be assumed for certain purposes to resemble in the electrostatic sense a rod charged equally and oppositely at opposite ends. Therefore a dipole. A Bohr model hydrogen molecule on the other hand assumes two electrons opposite one another in the same orbit and revolving midway between two positive charges. There are then four charges in the molecule which may be regarded as forming two dipoles situated relative to one another in a manner to more or less compensate their respective moments and constituting a quadrupole. The simplest model of an octapole molecule would possibly be a positive charge, equivalent to the total charge of eight electrons, at the center of a cube each corner of the cube containing one electron.

It is not improbable that a molecule at small densities might behave as, for example, a quadrupole, and at higher densities differently, as regards polar order due to the mutual electrostatic disturbance which could occur as the molecules become crowded together. Dielectric constant measurements for simple type molecules in the adsorbed state, where they are tremendously "strained," might throw some light on the polarization changes to be expected at high molecular densities. Should considerable changes in polarization be observed in the adsorbed state as compared with the gaseous state, there would seem little doubt that the polar type of the molecule could not be regarded as independent of the density.

charge about which an electron rotates in a circular orbit. The figure represented (fig. 1) the simple negative electron of a hydrogen atom, as equivalent in effect to three hypothetical half charge negative particles and one half charge positive particle rotating about the positive nucleus at opposite ends of the orbit diameter (2a) as represented.⁷ From this representation it is clear that the rotating half charge electrons (angular vel. ω) may be considered in their electrical effect, to consist of a negative field associated with which is an oscillating dipole producing a pulsating field at any point without the atomic system (x, y, z). Consider next the nucleus as the center of a coördinate system

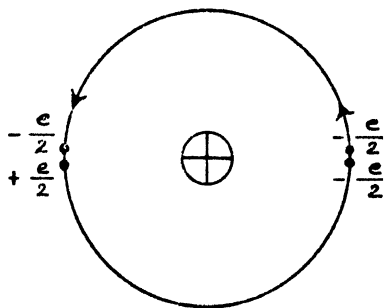


FIG. 1

(ϕ, θ, r) and fix attention first on the rotating dipole. Taking distances to x, y, z from $+e/2$ as r_1 and $-e/2$ as r_2 there is obtained for the potential at the point $x = r \sin \theta \cos \phi$; $y = r \sin \theta \sin \phi$; $z = r \cos \theta$

$$\Phi_1 = - \left[\frac{1}{2} \frac{e}{r_1} - \frac{1}{2} \frac{e}{r_2} \right]$$

But r_1 is the same as $(r \sin \theta \cos \phi^1 - a)^2 + y^2 + z^2)^{1/2}$
and r_2 the same as $(r \sin \theta \cos \phi^1 + a)^2 + y^2 + z^2)^{1/2}$ where

⁷ I owe this diagrammatic scheme to my colleague, Professor H. B. Phillips. The mode of representation is, of course, purely hypothetical. It is justified only to the extent that the calculation of the potentials of the negative and oscillating fields is facilitated.

ϕ^1 is taken equal to $(\phi - \omega t)$. To a first approximation $r_1 = r - a \sin \theta \cos \phi$ and $r_2 = r + a \sin \theta \cos \phi^1$ whereupon,

$$\Phi_1 = -\frac{ea}{r^2} \sin \theta \cos (\phi - \omega t)$$

which is Debye's equation for the pulsating potential. In a similar way the negative potential ϕ_2 becomes

$$\Phi_2 = \frac{ea^2}{r^3} \left(\frac{1}{2} - \frac{3}{4} \sin^2 \theta \right)$$

independent of the time. From the potential the average square of the electrical fields may be computed giving

$$\overline{E_1^2} = \frac{e^2 a^2}{r^6} \left(\frac{3}{2} \sin^2 \theta + 1 \right)$$

$$\overline{E_2^2} = \frac{9e^2 a^4}{4 r^8} \left(1 - 2 \sin^2 \theta + \frac{5}{4} \sin^4 \theta \right)$$

With the Bohr model at a distance $r = 10a$ the maximum value of $\overline{E_1^2}$ is 8×10^6 volts/cm. for E_2^2 , 0.76×10^6 . It results, therefore, that for this model the amplitude of the field fluctuation is over tenfold the time average field. It is further to be noted that E_1^2 preponderates more for great distances. The action of the time variable field on an outside electron has been computed and shown by Debye to result in the molecule's exerting on average a repulsive force on the electron. The repulsion of electrons (slow moving) on near approach to molecules is well known experimentally and the considerations reproduced above indicate how this effect comes into existence.

The question of the calculation of the repulsive action of the Debye forces in the case of two atoms or molecules requires evidently a knowledge of the electronic structure in much detail. Meanwhile, however, a considerable step has been taken in comprehending qualitatively how one molecule may reflect another on the basis of the modern electron structure assigned to atoms.

From what has preceded, the necessity is perceived of amplifying and adding to the specifications of the kinetic theory mole-

cule. The molecule must clearly be endowed with both attractive and repulsive forces obeying rather complicated laws. For some purposes or over restricted ranges of the variables, (i. e., temperature, pressure or both) it will possibly often suffice to assume simple inverse distance expressions; but experience alone can indicate to what extent and in which cases such simplifications remain a sufficient approximation in accounting for the various effects connected with molecular collisions or interactions generally.

THE MOLECULAR FIELD IN TRANSPORT PROBLEMS

The transport problems of the kinetic theory, viscosity, heat conduction, and diffusion are represented by the transfer, through the collisional phenomena, of momentum, energy and mass. Of the three the viscosity effect is of particularly great interest since it can be most easily measured accurately over a long temperature range.

A complete transport theory for other than the classical molecular model is complicated. The complication involved turns very largely on the fact, however, that we are ignorant of the law of molecular distribution for a gas in a steady state undergoing viscous action, as distinguished from a gas in the equilibrium state. Thus the Maxwellian distribution cannot be assumed to hold, for this law applies only to the case of a gas *in equilibrium*.

The classical molecular model was shown by Maxwell to lead to the prediction, somewhat surprising on first consideration, that the viscosity of a gas is independent of the density. This Maxwell himself proved experimentally.⁸ A further prediction, however, was that the viscosity varies as the square root of the absolute temperature. The latter prediction has been found emphatically not to be in accord with the facts for any gas at any temperature range thus far investigated.

The difficulty of the temperature dependence appeared to be

⁸ Boyle observed in his day that the time of oscillation of a pendulum was independent of the density of the air in which it was caused to operate which would be the case only if the viscous drag on the pendulum were independent of the density of the ambient air.

solved when the viscosity formula for a van der Waals' molecular model was computed by Sutherland (18) leading to a temperature dependence representable by $\frac{\sqrt{T}}{1 + \frac{C'}{T}}$. The quantity C

represents a quantity which is directly proportional to the work required to separate two molecules, of the hard sphere type, from contact to infinity. It is therefore closely related to the quantity a in van der Waals' equation.⁹ This has been shown in recent papers (19) (20) where the relation of C and a to the dielectric constant has been discussed.

If instead of a molecule of invariable diameter (index of repulsive force infinite) the viscosity formula is obtained for a molecular model possessing both repulsive and attractive fields the formula (6) has the form

$$\frac{\sqrt{T}}{\frac{1}{2} + \frac{C'}{T}}$$

where C' has the same physical significance as the coefficient C in the Sutherland formula. It may be noted that for n infinite in the more general formula there results the Sutherland form based on the hard sphere model.

The subsequent perfection attained in the experimental results for many gases combined with the extension of the measurements to lower temperatures, however, has shown two things. Firstly, the Sutherland formula fails to represent the viscosity data for many gases as lower temperatures are approached and secondly in the case of helium (21) it fails completely at all temperatures.

The general need of considering the molecular field in the theory of viscous action thus becomes evident. In fact, Maxwell himself had perceived that the difficulty of the temperature dependence resided in greater part, in the failure to take account of a

⁹ The a values with which C must be compared cannot in general be a as determined from critical constants but a value obtained from the gaseous compressibility data.

"molecular field effect." He developed the general equations for transfer phenomena, investigating, however, only the special case of points repelling as the inverse fifth power of the distance; an assumption which enabled him, due to the form of the fundamental equation, to dispense with a knowledge of the molecular distribution law. We owe to Enskog (22) (23) (24) and Chapman (25) the important results obtained by carrying the theory of gaseous viscosity to a definite and complete solution for each of the three molecular models; viz., the classical model, the van der Waals' and the point model repelling according to the formula $\lambda_n r^{-n}$. A further case has been partially investigated by Jones (6) who considers a molecule represented by a point and possessing both attracting and repelling fields of the type $\lambda_m r^{-m}$, $-\lambda_n r^{-n}$. It is sufficiently shown in the latter investigation that all the known facts concerning the temperature dependence of viscosity can be accounted for, if not entirely satisfactorily from a quantitative point of view, at least qualitatively. The position at present reached is then clearly that in general *both* the attractive field and the repulsive field must be considered in the kinetic theory. A final satisfactory knowledge of the molecular field depends, however, on a considerable extension of our knowledge of atomic and molecular structures combined at the same time, of course, with the discovery and development of a generalized dynamical theory.

DIELECTRIC CONSTANTS

Twenty years ago few physical chemists would have believed the special study of dielectric constants to have any direct relation to the major problems of their science. At present, however, there exists almost a "furor" for measuring the dielectric constants of gases and liquids which may readily be justified. The most important recent contribution to the theory of solutions (Debye-Hückel theory) makes considerations of the dielectric qualities of the solution system of fundamental importance, although for gases alone does a clear theoretical status exist. The interesting and important work on organic liquids at present being carried out, while as yet in many aspects uninterpretable theoretic-

cally, is nevertheless destined ultimately to have far reaching consequences.

The comments above have indicated that the cohesive pressure or the molecular attractive field is for quadrupole molecules, directly proportional to the Clausius-Mosotti constant.

$\left(\frac{D-1}{D+2} V = \frac{4}{3} \pi N \alpha = P_0.\right)$ In two recent papers (19) (20), the present writer has shown empirically that the constants for normal substances are simply related to the A and β constants of the equation of state and heats of adsorption. The characteristic of some molecules (polar compounds) of possessing a natural or permanent moment is of very great importance and the development of the theory by which the numerical values of the molecular dipole strength can be determined is of fundamental interest in enlarging the boundaries of the kinetic theory. A brief review of the physical ideas underlying the present theory is accordingly presented.

The theory of gaseous dielectric behavior which is most elegantly substantiated by the available experimental data is that of Debye, (26) (27) (28). The original theory was wholly classical in its theoretical setting. The subsequent attempts to give the theory a proper quantum "baptism" have been numerous, finally culminating in Pauli's treatment of the problem by the matrix mechanics which results in an expression reducing for higher temperatures to Debye's original formula.

The Debye theory is based on simple, physical ideas. The experimental data indicated long ago that substances, in their dielectric behavior, may be classified into two groups, those for which the function $\frac{D-1}{D+2} V$ (Clausius-Mosotti expression) (D dielectric constant, V molecular volume) is constant and those for which it is not. Now the theory leading to the expression $\frac{D-1}{D+2} V = \text{constant}$ is readily derivable, assuming the presence of a movable electron in the molecule and that the external electric field in which the gas is brought induces an electric

moment in the molecules composing the gas. Proportionality between the induced polarization of the molecules and all values of the field strength is also assumed. Debye gave the solution of the following problem: assume a molecule capable of becoming inductively polarized and superpose thereon the effect, in the actual state of movement of the molecules as conceived in the gaseous state, a *permanent* or *natural* dipole moment having a fixed position in the molecule. It is clear that in an electric field the latter kind of molecules will tend to align themselves in the field with the axis of the natural moment in the direction of the field. But the aligning tendency is interfered with the higher the temperature becomes because of the motion and collisions of the molecules. Thus for very high temperatures the aligning tendency would be almost completely destroyed. The contribution, therefore, of the natural dipole to the dielectric constant formula should be representable by a term or terms containing inverse temperatures. A formula containing a first approximation for the *dipole* term would be given by the following expression:

$$\frac{D-1}{D+2} V = \text{constant} + \frac{a}{T}$$

The computation of a , using the ordinary probability theory (29) to calculate the number of molecules whose axes make an angle in the range $d\theta$ with the field direction, gives $a = \frac{4}{9} \frac{\pi N \mu^2}{k}$

where N is Avogadro's number, μ the value of the permanent natural electric moment and k Boltzmann's constant.

Exactly what character of atomic structure can lead to a natural electric or dipole moment is not known, otherwise it would be possible to compute μ . Meanwhile values of a may be determined from observational material and μ computed. The values of μ thus obtained are largest for hydrochloric acid gas, water, the alcohols, and in general a temperature dependence of the Clausius-Mosotti expression is found for those substances which, from certain aspects of their chemical behavior, chemists had

long ago designated as "polar" compounds or "associated" compounds.

With the assistance of a knowledge of the magnitude of the permanent moments it is possible to construct a purely electrical theory for the representation and correlation of the facts concerning certain liquid mixtures (associated substances) such as, for example, the freezing points and boiling points. Such a theory may be viewed indeed as a logical extension of the well known Debye-Hückel theory of ionic solutions. A few details regarding the treatment of liquid mixtures from this point of view are to be found in Debye's article on "Dielectric Constants and Association" in the sixth volume of the *Marx's Radiology*. The present paper merely calls attention to the fact that a further development of the theory of non-aqueous solutions from the point of view suggested by Debye cannot fail to be more satisfactory, more general and fruitful in guiding further experimental research in a profitable direction than the special explanations hitherto advanced to explain certain "anomalies" in liquid mixtures.

THE REFRACTIVE INDEX AND SCATTERING OF LIGHT

The older classical theory has already been referred to in relation to the refractive index in the discussion of which it is sufficient for purposes of orientation, to assume merely that the electrons in the molecule are displaceable from their equilibrium positions under the action of the external forces. The theory of such effects as ordinary dispersion and anomalous dispersion offers difficulties, however, when the assumption is made that the electrons are moving in orbits, for here we do not have equilibrium positions for the electrons. It may be assumed, nevertheless, that a perturbation or shifting of the orbits takes place due to the action of the light or an electric field although the precise details are complicated by the mutual inter-relation of the other orbits. In a simple case it is readily perceived that the deviation or wobbling of the orbit from its original form will constitute a virtual electric moment and the observable effects of the action of light produced in gases may be assumed due to the rate of

change of a virtual electric moment. The relation of refractivity to the dielectric constant is important and in many gases ("non-polar") the index of refraction for long wave lengths is equal to the square root of the dielectric constant.

A theory of dispersion has been developed by Debye (30) for the case of the Bohr hydrogen molecule on the basis of a periodic wobbling of the orbits responsive to the external periodic force of the electric vector of the light beam. Debye deduces from this periodic disturbance of the original motion of the electrons, the index of the refraction of hydrogen as a function of the wave length. On comparison with experiment (31) it is found that the calculated index is in agreement for wave lengths in the visible regions but there occurs a progressive deviation at shorter wave lengths. In the ultra-violet region the deviations are considerable, which might be expected in view of the limitation of infinitely small disturbance of the orbits assumed in computing the refractive index formula. Moreover, it is well known that in the ultra-violet absorption takes place disrupting the hydrogen molecule. The classical basis upon which the calculations rest would of course cease to be sufficient as a basis for discussing the phenomena when absorption takes place. In fact it is precisely the matter of absorption which has constituted a grave difficulty in the older theories and which constitutes an even more formidable difficulty in considering the phenomena on the basis of Bohr's model. It is true Bohr has given, for his molecular model, some noteworthy explanations of absorption particularly for those special cases of resonance and fluorescence.

One remark should be added concerning Debye's formula for the refraction of hydrogen. The formula for $(n^2 - 1)$ contains several terms of which three have the form $Ne^2 / m (\nu_0^2 - \nu^2)$ where the denominator contains the difference between the square of the incident frequency and ν_0^2 a quantity characterizing the vibrations of the molecule. There are, however, two more terms in which instead of the difference of two frequencies there enters the *sum*, showing that they correspond to degrees of freedom for which the motion is *unstable* (32). Lorentz (33) has given expression to the difficulty by stating "it is just as if you

wanted a pendulum to vibrate about a position of unstable equilibrium in which it stands vertically upward." Attempts to improve the theoretical position of the subject have been made recently by several European investigators. (34) (35) (36) (37) (38) (39) (40) (41).

The so called scattering of light is closely related to the dispersion problem as discussed above for which Rayleigh deduced (assuming the molecules to constitute a perfect gas) the well known formula,

$$h = \frac{32}{3} \frac{\pi^2}{N \lambda^4} \frac{(n^2 - 1)^2}{Idx} = - \frac{dI}{I dx}$$

where $\frac{dI}{I}$ is numerically the percentage change in the intensity of the beam of light when traversing a layer of unit thickness. Since h varies inversely as λ^4 , the scattering will increase in the direction of smaller wave lengths; an effect which as we well know accounts for the blue color of the sky. The theory of the scattering for long waves¹⁰ may be given in a quite different form in which the basis of the consideration involves essentially the use of the ordinary probability theory in computing the fluctuations in density of the gas. Since the refractive index varies with density the gas is to be regarded as inhomogeneous for a periodic disturbance such as light. Scattering of the light thus occurs and the Rayleigh formula is again obtained with, however, the important difference that the von Smoluchowski's (42) expression is more general not being restricted to a perfect gas. It can therefore be applied to the critical condition of a fluid, providing an explanation of the critical opalescence.

¹⁰ "Long waves" refers to a magnitude large as compared to the average distance between molecules in a substance. Thus green light is of wave length 5600×10^{-8} cm. whereas in a gas at 0° and one atm. the average distance of the centers of molecules is 33.3×10^{-8} and the condition of "long waves" is therefore fulfilled. In a regular crystal, the even spacing of the molecules would produce no scattering (transparency) until the wave length of the incident light became of the same order of magnitude as the distance between atomic centers (2 to 3×10^{-8} cm.). Waves of such length are obtained from the x-ray tube which give scattering from crystal planes, the intensity of which is exceedingly strong in definite directions as first shown by Laue.

The aspect of light scattering phenomena of most interest to the physical chemist is connected with the polarization relations of the incident and scattered light. According to the original Rayleigh theory a plane polarized incident beam should be accompanied by plane polarized light in the scattered light. If, on the other hand, the incident beam is heterogeneous the scattered light will be partially polarized, yielding two components each of equal mean intensity. The observation of the actual polarization discloses, however, that this is true for but few gases leading to the inference that the molecule is not electrically spherically symmetrical. Thus argon and neon show the simple behavior predictable from Rayleigh's formula, thereby implying a high degree of symmetry in the electronic structure of these atoms, whereas helium appears to be unsymmetrical.

Under the circumstances the obvious addition to make to the theory is to assume, in a phenomenological manner, that the molecule possesses a different electric moment, responsive to the light vector for each axis (m_x , m_y , m_z). The molecules will evidently orientate in every direction in the course of their movements in the gaseous state and by a somewhat more complicated procedure than Rayleigh employed there results a general formula, which for incident light propagated along the z axis, gives for the ratio of the intensity of the light parallel to the incident beam (S_p) to that perpendicular to the incident beam (S_s) an expression which depends on b_{11} , b_{22} , b_{33} , the principal "anisotropic" coefficients of the molecular moments corresponding to the axes x , y , z . Thus designating by R (43) the ratio of S_p to S_s , there results the equation:

$$\frac{10}{6-7} \frac{R}{R} = \frac{(b_{11} - b_{22})^2 + (b_{22} - b_{33})^2 + (b_{33} - b_{11})^2}{(b_{11} + b_{22} + b_{33})^2}$$

an expression which vanishes for $b_{11} = b_{22} = b_{33}$ (i.e., a molecule symmetrical in the sense proposed). A few data are given in table 1 taken from Debye's article in Marx Handbuch der Radiologie.

The result of surprising interest is that helium shows a defect in symmetry larger than for any of the other gases of the table.

The fact that for N_2 , R is twice that for CO is significant of a difference which would not have been inferred since these two gases show a surprisingly close parallelism in their physical characteristics. Benzene is more asymmetrical than might have been supposed by one familiar with its organic chemical properties.

Clearly the scattering of light should be further investigated for a wide variety of substances since the phenomenon affords a very direct approach to an enlarged knowledge of molecular anisotropy. Thus the organic compounds have been assigned very definite molecular structures which should be related (44) to the indications regarding molecular character deducible from light scattering data.

TABLE 1

SUBSTANCE	$S_p/S_s = R$
H_2	0 022
He.....	0 42
A.....	0 00
Ne.....	0 01
N_2	0 037
O_2	0 064
C_2H_2	0.12
C_6H_6	0 06
NO	0 026
N_2O	0 122
CO.....	0 017
CO_2	0 098

ELECTRIC DOUBLE REFRACTION IN GASES AND LIQUIDS

Kerr, some fifty years ago, found that carbon bisulfide became double refracting for a light ray perpendicular to an electrostatic field in which the liquid was placed. The amount of the effect was shown by Kerr to vary as the square of the field strength. The analogous effect in the magnetic case was observed by Cotton and Moulton (45). The experimental arrangement for demonstrating the effect consists essentially of a pair of metal plates with means of applying a potential, and a pair of Nicol prisms. In figure 2 the plates + and - are introduced into the carbon bisulfide and a ray of plane polarized light passed through

the liquid parallel to the metal plates. One of the Nicol prisms, n_1n_1 , is placed before the plates, the other, n_2n_2 , after the plates in such a way that the principal planes of the prisms are included at 45° to the field direction. With such an experimental arrangement no light will pass in the absence of a field with an isotropic liquid between the plates. Kerr found that light would pass when an electric field was established between the plates thus demonstrating a state of "electric strain" suffered by the molecules under the action of the field. The magnitude of the double refraction has been found to diminish greatly with temperature increase.

The type of theory which is at present in best accord with the experimental facts makes use of the Langevin orientation theory

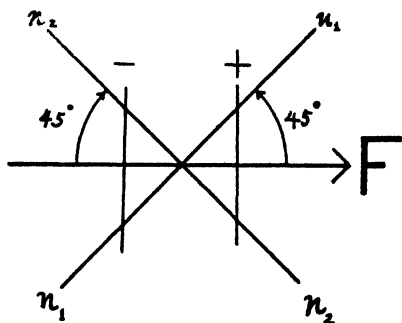


FIG. 2

(29) with a polarizable molecule assumed to have different properties in different directions. Two cases are distinguishable, that in which the molecules are susceptible of an inducing action of the field and electric vector of the light beam only, and that in which the latter effect is combined with the effect due to a natural dipole analogously as in the theory of dielectric constants. The theoretical mode of treatment is statistical and the classical probability theory has been used with the assumption that the molecules are completely anisotropic (for illustration, a flattened ellipsoid as compared with the sphere). The relation of anisotropy to molecular structure is a subject about which much remains to

be learned, moreover the development of the theory of the Kerr effect deserves continued attention (46) (47) (48) (49).

The general formula for the Kerr effect is as follows, where K is the constant, n_p the index of refraction for the ray vibrating perpendicular to the field. The index of refraction for the normal liquid (wave length λ) may be denoted by n_o and the field intensity by E .

$$\frac{n_p - n_o}{n_o} = KE^2 = B \frac{\lambda}{n_o} E^2 \quad (1)$$

$$K = B \text{ (a constant) } \lambda/n_o$$

The theoretical problem centers on the computation of the indices n_p and n_o and, as already stated, the model of the molecule which appears to be fairly satisfactory is that which is assumed to be polarizable differently in different directions, and, in the general case, possesses in addition a natural dipole moment.

The effect brings into evidence the fact that molecules are not spherically symmetrical in structure and this constitutes the reason for the special interest of the phenomena for physical chemistry. There are several aspects of this special interest, but the more obvious are perhaps the assistance a wide range of data for many substances will give, in supplying a definite and quantitative basis for the development of ideas regarding the forces which determine molecular structure and the molecular field. Evidently, it would be well to have also, for completeness, data regarding light scattering, dielectric constants, compressibilities and refractive indices. In recent years data regarding dielectric constants have been accumulating rather rapidly and to a lesser extent in the case of compressibilities. The data should be obtained over a wide range of temperature and density to be of maximum usefulness for theoretical purposes.

Returning to the fundamental formula of the Kerr effect, it will be useful in giving definiteness to the nature of the present theory to write down the expressions for n_p and n_o . Note should be made that the sign of the effect may be + or - or zero accordingly as $n_p > n_o$, $n_p < n_o$, $n_p = n_o$. For the refractive index

of the substance before applying the field, n_0 , there exists the formula of Lorentz

$$\frac{n_0^2 - 1}{n_0^2 + 2} = \frac{4\pi}{3} N_0 \frac{b_{11} + b_{22} + b_{33}}{3}$$

where N_0 is the number of molecules in unit volume and b_{11} , b_{22} , b_{33} are the coefficients¹¹ of the components of the polarizability of the molecule for the *light vector*.

For the ray vibrating parallel to the static field, n_p , and perpendicular thereto, n_s , there may be written

$$\frac{n_p^2 - 1}{n_p^2 + 2} = \frac{4\pi}{3} N P_s$$

and

$$\frac{n_s^2 - 1}{n_s^2 + 2} = \frac{4\pi}{3} N P_z$$

The expressions for P_s and P_z are as follows (43) where Z_0 is the strength of the static field:

$$P_s = P_0 + (\theta_1 + \theta_2) Z_0^2$$

$$P_z = P_0 + \frac{1}{2} (\theta_1 + \theta_2) Z_0^2$$

where $(b_{11} + b_{22} + b_{33}) / 3 = P_0$ and θ_1 and θ_2 have the following significance, μ_1 , μ_2 and μ_3 being the components of the natural dipole moment.

$$\theta_1 = \frac{1}{45 kT} [(a_{11} - a_{22}) (b_{11} - b_{22}) + (a_{22} - a_{33}) (b_{22} - b_{33}) + (a_{33} - a_{11}) (b_{33} - b_{11})]$$

$$\theta_2 = \frac{1}{45 kT^2} [(\mu_1^2 - \mu_2^2) (b_{11} - b_{22}) + (\mu_2^2 - \mu_3^2) (b_{22} - b_{33}) + (\mu_3^2 - \mu_1^2) (b_{33} - b_{11})]$$

There remains to consider the phenomenon of the volume change (or change in N_0) which may take place when a fluid is placed in an electric field (or magnetic field). The expression

¹¹ The analogous coefficients for the molecular polarizability due to the static electric field are denoted by the symbols a_{11} , a_{22} , a_{33} .

for the volume contraction is determined, aside from the strength of the field E by the change of the dielectric constant with pressure (50) and is as follows:

$$\frac{dv}{v} = \frac{1}{2} \left(\frac{dD}{dp} \right)_T \cdot E^2$$

The density of the fluid through which the light is passed in the Kerr experiment is therefore not constant but changed in proportion to the square of the strength of the field. Taking into account this fractional change in the number of molecules between the plates, the expression for 1 becomes

$$\frac{n_p - n_s}{n_0} = \frac{E^2}{36} (n_0^2 - 1) (n_0^2 + 2) (\theta_1 + \theta_2) (D + 2)^2 = K E \quad (\text{A})$$

The data available to 1920 has been collected and discussed from the point of view of their relation to chemical constitution by Kauffmann (51) and Leiser (52). For the purposes of the present paper it will be sufficient to refer to a few of the data for typical substances (see table 2).

It will be noted that for chloroform and aniline the constant is negative. The sign of the effect may be discussed from the point of view afforded by the equations for θ_1 and θ_2 . In the first place if no natural moment exists ($\mu_1 = 0$, $\mu_2 = 0$, $\mu_3 = 0$) the sign will depend upon θ_1 alone. The constant K depends then on a function of the a and b coefficients. It may be that these two coefficients are not very different (or proportional) numerically, at least in a region far from an absorption band. In the latter case θ_1 is a function of squares which means K will always be positive. In general a negative sign indicates that certain numerical relationship exists between the μ and b in the θ_2 expression.

The magnitudes of the average natural moment μ computed from the equation A, agree well with the similar quantity computed from the temperature dependence of the dielectric constant. Thus for HCl the Kerr constant gives 1.04×10^{-8} E.S.U. as against 1.03×10^{-8} E.S.U. from dielectric constant data.

Special interest attaches to an experimental method used by Pauthenier (53) whereby the field is applied and the light beam passed through the liquid simultaneously and in a time of the order of 10^{-6} to 10^{-7} sec. Now the density change in the liquid, due to the static field, requires a time for establishing itself which is measured by the speed of sound in the fluid. It is possible,

TABLE 2

SUBSTANCE	$K \frac{\text{cm}^2}{\text{Ergs}} \times 10^{12} \frac{20^\circ}{\lambda = 5893}$	D
N ₂ (gas).....	Negligible	Slightly greater than one
O ₂ (gas)	Negligible	
NO (gas).....	Negligible	
CO(gas)	Negligible	
CO ₂ (gas).....	24	
NH ₃ (gas)	59	Slightly greater than one
SO ₂ (gas)	167	
CH ₃ Cl (gas).....	545	
CH ₃ Br (gas)	820	
CHCl ₃ (liquid).....	-12.2	4.8
C ₆ H ₆ (liquid)	2.15	2.3
C ₆ H ₅ CH ₃ (liquid).....	2.73	2.4
C ₆ H ₅ Cl (liquid).....	32.7	5.7
C ₆ H ₅ Br (liquid)	32.7	5.2
C ₆ H ₅ NH ₂ (liquid)	-4.4	6.9
C ₆ H ₅ NO ₂ (liquid).....	+12.2	37.0
H ₂ O.....	14.4	80.5
CH ₃ OH.....	3.5	51.2
C ₂ H ₅ OH	2.8	25.8
C ₃ H ₇ OH.....	-9.1	22.2
Benzyl Alc.....	-55.8	13.0
CH ₃ COOH	17.8	

therefore, to arrange the experiment so that the period of the application of the field and the duration of the light is far less than the time for effecting a density change due to the field. The Kerr constant is under these circumstances given by a simpler expression than A wherein D is absent.

The case for double refraction in a magnetic field is in every respect similar to that of the static electric field.

COMMENTS ON THE EQUATION OF STATE PROBLEM

In the preceding part of the paper the attempt has been made to indicate the importance to Physical Chemistry of a knowledge of the molecular field. Various physical properties not usually considered by the physical chemist have, therefore, been briefly discussed because of the intimate connection which exists directly and indirectly between the important problem of the molecular field and these phenomena. As a concluding part of this paper a brief review of the Equation of State theory for pure gases will be presented. The latter problem is of fundamental practical importance and a brief discussion will illustrate the fundamental rôle that the molecular field plays in the theory. In addition, the relation of a few of the available experimental facts to the theoretical development will also be reviewed. This is the more important for the reason that by a careful consideration of the limitations of the theory of the equation of state in evaluating molecular constants from observational data, it becomes possible to interrelate the constants of the equation of state for gases to other fundamental physical constants, thus aiding in building up a better theoretical structure and decreasing the range of experimental data required for determining the molecular constants.

The limited range of the validity of the van der Waals' equation has already been touched upon and is indeed well known. These limitations, originate, as already indicated, from the use of an over simplified molecular model and a theoretical treatment leading to results valid at high temperatures and low pressures only. The van der Waals' equation, therefore, cannot possibly be expected to apply to actual substances in the liquid state, the critical state, or the highly compressed gaseous state. The precise meaning that should be attached to the constants a and b *determined from critical data* is in consequence by no means clear. The numerous attempts, therefore, to interrelate the a and b constants to molecular structure or other physical properties may be viewed as unpromising. Indeed, those apparent regularities which have been published, relating the constants a and b

to quantities deduced from other physical properties must be regarded as having little or no clear theoretical significance.

Admittedly, one of the outstanding theoretical difficulties at present confronting the physical chemist, is the doubtful *general* validity of classical statistical mechanics: probably, even when applied to problems involving only the energy of molecular translation. Nevertheless, there is an accumulation of evidence to indicate that at higher temperatures, the classical statistics are very approximately valid. As an illustration consider the recent Fermi (54) expression for a perfect gas at high temperatures,

$$pV = RT \left[1 + \frac{h^3 N}{16 (\pi m k)^{3/2}} \cdot \frac{1}{T^{3/2} V} + \dots \right]$$

Taking helium and using units of cc. per g., atm. there is obtained for the per cent deviation from the classical expression

$$\frac{p \bar{V} - RT}{RT} = \frac{70}{T^{3/2} V} 100.$$

At zero and one atm. the value of the deviation would be 2.8×10^{-4} per cent. At low temperatures the departure of the "Fermi" ideal gas from the classical ideal gas is marked, the pressure being given by an expression of the form

$$p = \frac{a}{V^{1/3}} + \frac{b T^2}{V^{4/3}}$$

where a and b are constants. Thus the pressure will vanish only for v infinite at $T = 0$, otherwise a positive pressure exists. This implies that the energy is finite at absolute zero and the heat capacity at constant volume vanishes at zero.

The expectation may be entertained, therefore, that the classical statistics may be applied where high temperatures are in question and higher molecular weight substances¹² are concerned.

¹² The expression for the deviation of the "Fermi" perfect gas from the classical varies inversely as the (mol. wt.)^{3/2}. This would mean a very large deviation for a so-called "electron gas" and correspondingly higher temperatures would have to be considered for negligible deviations from the classical perfect gas state.

When, however, the liquid phase is formed it is by no means clear that the classical mechanics will suffice even if the calculation of the equation of state for such a highly condensed phase could be carried out.

There are several methods (7) (9) (10) (13) (14) (55) (56) (57) of using the classical mechanics to deduce the equation of state, all of which are, from a theoretical point of view, equivalent. The use of the Gibbs's equations of statistical mechanics, however, appears to make somewhat more evident the nature of some of the approximations which must inevitably be made in securing a definite result from such calculations. The equation 93 of Gibbs may be made the starting point,

$$\int \dots \int e^{\frac{\psi - \epsilon}{\theta}} dp_1 \dots dq_n$$

where ψ may be considered a constant for a definite or constant value of θ . The latter quantity will be assumed equal to kT where k is Boltzmann's constant and T the absolute temperature as defined by a gas thermometer employing an actual gas, where the temperature readings are obtained by conducting measurements in such a manner as to give, by extrapolation, readings referred to the gas at infinitely low pressures. The quantity ϵ is the energy of a molecular system while the p 's and q 's represent the momenta and coordinates of the molecules characterized by values of ϵ , ψ and θ . The equation 93 integrated over all the phase-space must give the total number of molecular systems and accordingly it is permissible to write (Gibbs Eq. 105).

$$e^{-\frac{\psi}{kT}} = \int \dots \int e^{-\frac{\epsilon}{kT}} dp_1 \dots dq_n \quad (1)$$

Gibbs shows that ψ may be identified with the free energy defined by the thermodynamical equation $F = U - TS$ where U is the internal energy and S the entropy. There results finally the equation for the free energy which may be written as follows:

$$\psi = -kT \log \int \dots \int e^{-\frac{\epsilon}{kT}} dp_1 \dots dq_n \quad (2)$$

The equation of state follows at once from this equation, provided the indicated integrations can be effected, since $\left(\frac{\partial \psi}{\partial v}\right)_T = -p$.

The integrations will be affected for two cases, one in which the van der Waals' molecular model is assumed where the attractive force¹³ is represented by $\lambda_m r^{-m}$ and also for a point molecule possessing a spherically symmetrical repulsive field $-\lambda_n r^{-n}$.

We begin the calculation of the integral by allowing the momentum increment dp of each molecule to be represented by $m^3 dx dy dz$, ϵ , by $\frac{1}{2} m (\dot{x}^2 + \dot{y}^2 + \dot{z}^2) + (\phi_m)$, where x , y , z , are the velocity components and ϕ_m is the potential energy due to the attractive field (van der Waals' molecular model). The free energy equation then becomes

$$\psi = -kT \log \left[(2 \pi m kT)^{\frac{3N}{2}} \int \dots \int e^{-\frac{\phi_m}{kT}} dx_1 dy_1 dz_1 \dots \right] \quad (3)$$

where the dq 's have been replaced by $dx dy dz$.

The treatment of the remaining integral requires that ϕ_m shall be known as a function of x , y , and z , and due allowance must also be made for the fact that certain portions of the space V containing the molecules are excluded because of the finite volume, $\frac{1}{2} \pi d^3$ or δ of each molecule. The gas will be assumed sufficiently dilute that only double collisions need be considered.

$$\int \dots \int e^{-\frac{\phi_m}{kT}} dx_1 dy_1 dz_1 \dots = \int \dots \int \left[1 + \left(e^{-\frac{\phi_m}{kT}} - 1 \right) \right] dx_1 dy_1 dz_1 \quad (4)$$

Consider the molecules to be introduced into the volume V one at a time. For the first molecule it is clear that no portion of the space requires exclusion since the whole volume is available for its action and no potential energy is involved. The second molecule added to the space finds a portion of the space excluded and the potential energy enters the consideration.

¹³ Reference has already been made to the fact that the molecular field cannot, on the basis of what is already known about atomic and molecular structure, be represented by a single inverse distance expression. Several terms may be necessary depending on the substance and the nature of the phenomena to be accounted for.

Regarding one of the two molecules as a point and the other as of diameter $2d$ it is perceived that the space to be excluded for the action of the two molecules is $\frac{1}{6} \pi (2d)^3$ or $\frac{4}{3} \pi d^3 = 8\delta$. The third molecule added results in $2 \times \frac{4}{3} \pi d^3$ being excluded from the whole volume and similarly for the remaining molecules to the N minus first. The integral in (4) with these considerations applied becomes, if for brevity, the integral

$$\int \left(e^{-\frac{\varphi_m}{kT}} - 1 \right) dx_1 dy_1 dz_1 \dots$$

is denoted by I ;

$$V [V - (8\delta - I)] [V - 2(8\delta - I)] [V - 3(8\delta - I)] \dots [V - (N-1)(8\delta - I)]$$

The expression for (3) is now written:

$$\begin{aligned} \psi = -kT \log \left(2 m k T^{-\frac{3}{2}} \right) - kT \{ \log V + \log [V - (8\delta - I)] + \dots \\ + \log [V - (N-1)(8\delta - I)] \} \end{aligned} \quad (5)$$

The value of p is easily obtained from (5) with the following result:

$$\begin{aligned} p = kT \left[\frac{\partial}{\partial v} \log V + \frac{\partial}{\partial v} \log V \left(1 - \frac{8\delta - I}{V} \right) + \dots + \frac{\partial}{\partial v} \log V \right. \\ \left. \left(1 - \frac{(N-1)(8\delta - I)}{V} \right) \right] = \frac{NkT}{V} - \frac{N^2 kT}{2 V^2} (8\delta - I) \end{aligned}$$

The evaluation of I requires that φ_m be given in terms of the distance between two molecules and Debye's molecular quadrupole potential $-\frac{3}{r^3} \frac{\alpha \tau^2}{r^3}$ may be assumed. The integral I becomes, where the integration is to be carried out from the smallest distance of approach (d) to infinity,

$$I = \int \left(e^{\frac{3\alpha\tau^2}{r^3}} - 1 \right) dv = 4\pi \int_d^\infty \left(e^{\frac{3\alpha\tau^2}{r^3}} - 1 \right) r^2 dr.$$

The evaluation of the integral is easily accomplished by expanding the exponential term with the result

$$I = \frac{4 \cdot 3 \pi \alpha \tau^2}{5} \cdot \frac{1}{dT} + \dots \frac{4 \cdot 3^i \pi}{i! (8i-3)} \left(\frac{\alpha \tau^2}{d^3} \right)^i \left(\frac{1}{d^3} \right)^{i-1} \frac{1}{(kT)^2} \quad (6)$$

The final equation for p is, writing for Nk the symbol R , β for $4(N\delta)$, the fourfold volume of all the N molecules,¹⁴ and A for $\frac{6}{5} \frac{\pi N^2 \alpha \tau^2}{d^3}$

$$p = \frac{RT}{V} + \frac{RT}{V^2} \left[\beta - \frac{A}{RT} \left\{ 1 + \frac{25}{78} \frac{A}{\beta RT} \cdots + \frac{5^i}{i! (8i-3) 3^{i-1}} \left(\frac{A}{\beta RT} \right)^{i-1} \right\} \right] \quad (7)$$

The bracketed member of the third term of the right member represents the "aggregation effect" or "clustering tendency" of the molecules which only becomes negligible at high temperatures. Neglecting the series terms the equation may also be written as follows:

$$p = \frac{RT}{v - \beta} - \frac{A}{v^2}$$

which is the van der Waals' form.

The derivation given may be regarded as entirely rigorous under the conditions assumed, namely the validity of the classical mechanics and not too high pressures. It remains to indicate briefly how this equation corresponds with the experimental facts. We may begin by writing the equation in a somewhat different form where $f \left(\frac{1}{T} \right)$ represents the series terms of the brackets in (7);

$$pV = RT + RTB \frac{1}{V} = RT + \frac{RT}{V} \left[\beta - \frac{A}{RT} \left(1 + f \frac{1}{T} \right) \right]$$

$$B = \beta - \frac{A}{RT} \left(1 + f \frac{1}{T} \right) \quad (8)$$

The coefficient B has been referred to by continental writers as the second "virial" coefficient and may be easily determined at each temperature for which observational data exists. According to (8) the values of B should tend to become linear in T^{-1} as higher temperatures are approached. The figure 3 contains the B data for hydrogen, helium and nitrogen plotted with

¹⁴ This expression for A is identical with that obtained by Debye, *Physik. Z.* 21, 1 (1920).

corresponding values of T^{-1} on the axis of abscissae. Evidently none of these gases appear to be approaching a condition at the high temperatures where B is linear in T^{-1} .¹⁵ On the contrary the helium B coefficients pass through a maximum, while the nitro-

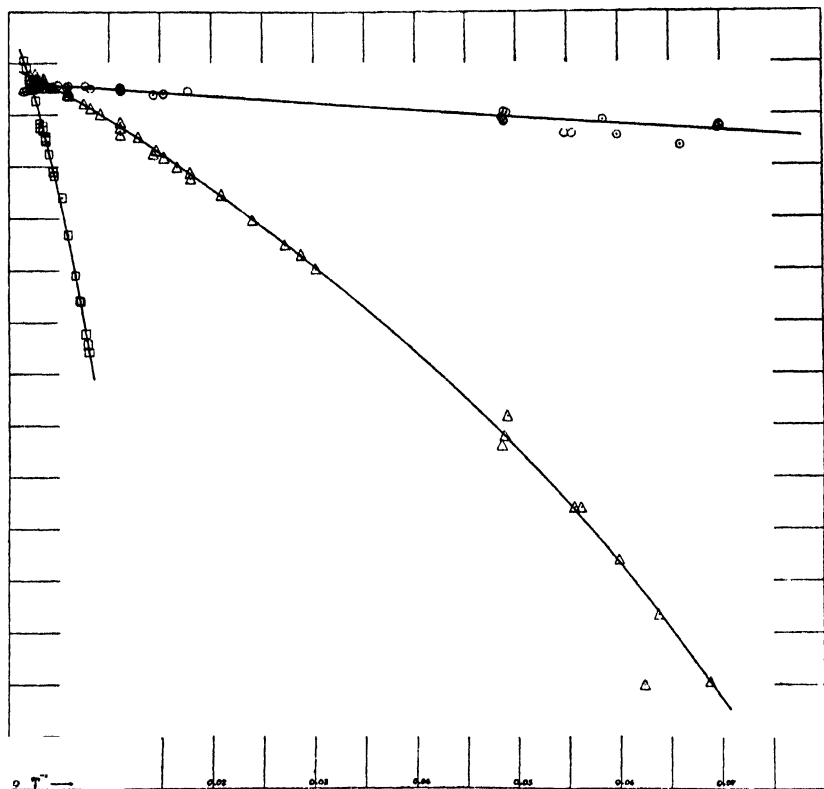


FIG. 3. THE OBSERVED EQUATION OF STATE DENSITY COEFFICIENTS FOR HELIUM \circ , HYDROGEN Δ AND NITROGEN \square RELATED TO TEMPERATURE AS INDICATED BY VAN DER WAALS' EQUATION

The data should be representable by a straight line in the diagram, provided van der Waals' equation was valid.

gen coefficients show a relatively much slighter tendency to curve toward the B axis above 200° . The conclusion to be drawn

¹⁵ This state of a gas, linear relation of B to T^{-1} , may be conveniently denoted as the "van der Waals' state."

is therefore that instead of B approaching the limiting value β for $T^{-1} = 0$ the actual course of the curve may be interpreted to indicate that β becomes progressively smaller with increasing temperature. The case of nitrogen (58) has been discussed elsewhere, but it may be noted that for this gas the magnitude of A

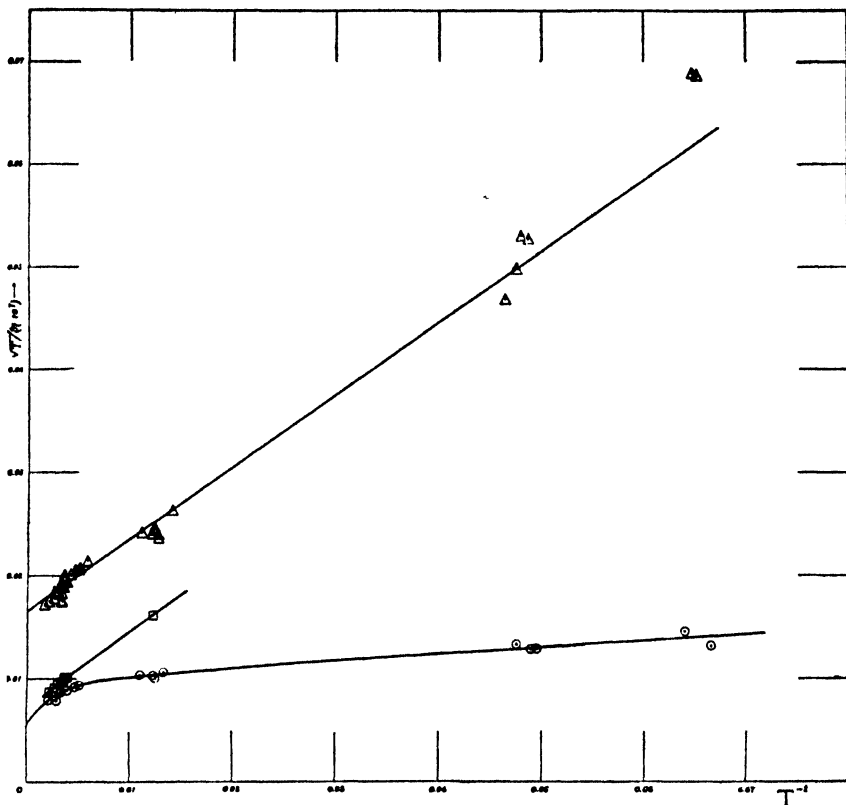


FIG. 4. THE VISCOSITY OF HELIUM \circ , HYDROGEN Δ , AND NITROGEN \square AS A FUNCTION OF TEMPERATURE ACCORDING TO SUTHERLAND'S FORMULA

relative to β is so large that a correspondingly higher temperature is required to reach a maximum as compared with helium, which has an A value smaller than for any other substance.

It is apropos at this point to examine other data for the purpose of determining whether other experimental facts indicate that the

apparent molecular diameter must be regarded as variable with temperature. The viscosity of a gas is a property, the theory of which has been worked out for a van der Waals' molecular model

(23). In terms of $\beta = 2/3 \pi N d^3$ and $A = \frac{6}{5} \pi N^2 \frac{\alpha \tau^2}{d^6}$ the equation may be written as follows; Where M is the molecular weight and k Boltzman's constant.

$$\eta = 3 \cdot 159 \cdot 10^{-5} \frac{\sqrt{MT}}{\beta^{2/3} \left(1 + 0 \cdot 2745 \frac{A}{\beta RT} \right)} \quad (9)$$

The latter equation indicates that $\frac{\sqrt{T}}{\eta}$ should be linear in T^{-1} and the data for the three gases used for the discussion above are presented in figure 4. Evidently the viscosity of helium shows no tendency, particularly at high temperatures, to be related to the temperature as indicated by formula (9). Nitrogen on the other hand is tolerably represented and an examination of all available viscosity data indicates that the formula (9) represents the data (19) well, particularly at higher temperatures.

Another model of the molecule for which the viscosity formula has been rigorously derived is that of a point repelling as an inverse power of the distance. The formula taken from Enskog's dissertation is as follows, where a is a number slightly greater than 1, depending only on the index of the distance in the repulsive force formula $F = \frac{C}{r^a}$, M is the molecular weight, Γ is the gamma function symbol and N is Avogadro's number

$$\eta = a_\nu \left(\frac{2 RT}{NC} \right)^{\frac{1}{\nu-1}} \frac{15 \sqrt{M RT}}{16 \sqrt{\pi} \Gamma \left(\frac{3\nu-5}{\nu-1} \right)} \quad (10)$$

This formula may be written in the form $\eta = G T^{\frac{\nu+3}{2(\nu-1)}}$ and in figure 5 the values of $\log \eta$ for helium have been plotted with the corresponding values of $\log T$. Evidently the form of the

function in (10) suffices to represent the data fairly satisfactorily. The value of ν , the index of the repulsive force may be obtained from slope of the line drawn through the data and is close to 15. The inference which seems to follow is that, at least for helium, the notion of a hard molecule of invariable diameter must be abandoned as a model and replaced by one possessing a repulsive field as well as an attractive field.

The distance of closest approach in a gas phase composed of repelling particles, must vary with the kinetic energy (temperature) as discussed in the first part of the present paper. The equation of state is in fact easily deduced for a low pressure gas whose A constant is small enough to be neglected (helium) at high temperatures.

Proceeding as before to calculate ψ the equation of state is found to be¹⁶

$$pV = RT + \frac{RT}{V} \frac{\beta_0}{T^{\nu-1}} \quad (11)$$

The equation (11) may be regarded as sufficiently approximate for helium at high temperatures where the attractive term of the order of $\frac{A}{RT}$ is very small by comparison with $\beta_0/T^{3/\nu-1}$. It is perceived that the logarithm of the B coefficients for helium at the highest temperatures, may be plotted with $\log T$ and an estimate thereby obtained of ν . It results that ν is approximately 15 in agreement with the value of the index obtained from a consideration of the viscosity dependence on temperature. The conclusion is supported that the molecular field must be assumed,

$$^{16} = kT \log (2 \pi mk)^{\frac{3\nu}{2}} [V(V-I)(V-21) \dots]$$

$$\text{where } I = \int_0^\infty \left(e^{-\frac{\lambda}{r^{\nu-1} kT}} - 1 \right) dx dy dz$$

where ν is the index of the distance in the law of repulsive force and λ is a constant involving the constant of repulsive force. The quantity $\beta_0/T^{3/\nu-1}$ may be considered to be equivalent to $2/3 \pi N(\bar{d})^3$ where \bar{d} is the apparent diameter of a molecule at definite temperature.

(at least for helium) to possess both an attractive and a repulsive character acting simultaneously.

Further light on the viscosity temperature dependence is obtained by inspecting the formula of J. E. Jones (6), who has

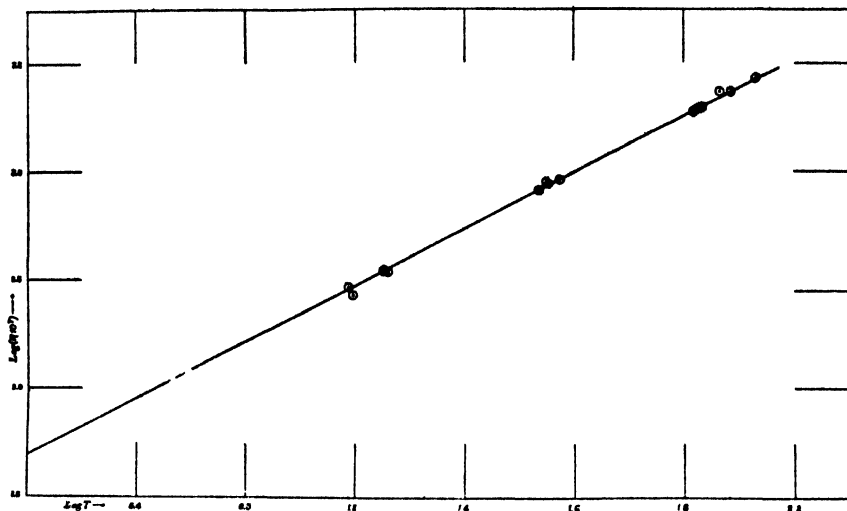


FIG. 5. LOGARITHM OF THE VISCOSITY AS A FUNCTION OF THE LOGARITHM OF THE ABSOLUTE TEMPERATURE FOR HELIUM

developed a formula for the case of a point molecule possessing both attractive and repulsive fields. The formula follows:

$$\frac{\sqrt{T}}{T^{-\frac{2}{\nu-1}} + \frac{C}{T}} \quad (12)$$

In this formula $T^{1/2}$ is the temperature dependence for the classical molecular model, $T^{-\frac{2}{\nu-1}}$ represents the effect due to the repulsive field while C/T is representative of the attractive field.

Evidently when ν is large $T^{-\frac{2}{\nu-1}}$ varies slowly at higher temperatures. On the other hand if C is also large (Nitrogen) the temperature dependence will be determined, largely by the term C/T and \sqrt{T} . With helium C is very small (4 to 5 units as

compared with about 100 for Nitrogen) and consequently the temperature dependence is determined by $T^{-\frac{2}{r-1}}$ and \sqrt{T} .

The equation of state may be derived by the method used above in which spherically symmetrical attractive and repulsive fields are both assumed. Such a calculation has been carried out by J. E. Jones (59) by a method which fundamentally does not differ from that employed in the present paper. Assuming the molecule to be of the quadruple type and repelling as the inverse fifteenth power, I find the following equation where τ is written for $T^{3/14}$ and β_0 and A_0 are constants:

$$pV = RT + \frac{RT}{V} \left[\frac{\beta_0}{\tau} - \frac{A_0}{R\tau^3} - 0.4638 \frac{A_0^2}{R^2 \beta_0 \tau^5} - 0.2893 \frac{A_0^3}{R^2 \beta_0^2 \tau^7} \dots \right] \quad (13)$$

This equation represents the data for helium, hydrogen and nitrogen well at low pressures and high temperatures which is not the case with any equation which predicts a linear increase of pressure with temperature as a limiting condition for temperatures approaching affinity.¹⁷

The scope of the present paper precludes a complete discussion of the important question of the equation of state of natural dipole gases. The potential energy (attractive) in the case of the later gases must be represented by at least two terms, one representing the potential due to the dipole and the other due to the "induced" polarization as for non polar substances. It may

¹⁷ Only during the past few years have observations on the p , v , T properties been carried to high temperatures (400°). Previously the data for only a few substances extended even to 200°. With this temperature (200°) as an upper limit it formerly appeared clear that all substances (except helium) were approaching a condition where the pressure increased linearly with temperature. The temperatures at which measurements must be carried out to show the high temperature maximum in the virial coefficient or even a tendency in this direction are higher the larger the value of A or the attractive constant, for the molecule. Thus with nitrogen the effect is just perceptible between 200° and 400°. The temperature in the case of the latter gas at which a maximum would be experimentally demonstrable is estimated to be about 3000°. The theoretical importance of the effect is not, however, of minor importance even in this case, for failure to allow for the effect (temperature variability of apparent molecular diameter) is sufficient above 200° to introduce considerable error in the calculation of pressures.

be remarked, however, that the permanent dipole contribution to the "cohesive pressure" would tend to vanish with temperature increase analogously as in the dielectric constant formula and for the same reasons. The "cohesive pressure" due to the induced polarization would remain operative at all temperatures as indicated by formula (7).

The brief reference to the relation of some of the data to the theoretical formulas for the viscosity and Equation of State derived by the use of very rudimentary and incomplete expressions for the molecular field serve merely as simple illustrations of the far reaching importance of a more exact knowledge of the molecular field. There is indeed scarcely a branch of physical chemistry which would not be benefited by an improved knowledge of the mode of action and properties of these molecular forces.

The explicit discussion attempted above has centered on the conception of a molecular field assumed to be spherically symmetrical. For the equation of state problem, gaseous viscosity, heat conduction, diffusion etc., this assumption is quite justified since the molecules are rapidly rotating and thus the field in its action is "averaged" and consequently is satisfactorily represented by an assumed symmetry. While this condition of assumed symmetry suffices for describing the properties of a *pure* gaseous phase, there are reasons worth considering for supposing the disposition of the field to be unsymmetrical and selective in the case of certain mixtures. How else may the reactive tendency of certain gaseous mixtures be explained, such for example as hydrochloric acid gas and ammonia gas? Also the special facts observed in connection with adsorption, catalytic phenomena and surface tension indicate a very striking selective action in the operation of the molecular field. In the liquid phase also the different solubility phenomena are direct evidence of the highly selective character of the molecular field.

The discussion of light scattering and the Kerr effect has perhaps indicated sufficiently the fact that molecules in general have different properties in different directions. There can scarcely be any doubt that further and more complete investiga-

tions of these effects for pure substances and mixtures, for both the gaseous and liquid phase,¹⁸ combined with a correlation of the quantitative results with other physico-chemical data will yield results of the highest interest to the progress of chemistry.

The interesting and important observations relating to surface tensions, particularly the observations made relating to films of the fatty acids etc., are of great interest from the point of view of the molecular field. The development of a quantitative theory of the kinetic kind is, however, extremely difficult. It is safe to say that a flood of light will be thrown on many aspects of the molecular field problem when such a theory is formulated and used to interpret the mass of available data.

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¹⁸ Raman (60) has recently observed a striking phenomenon in the character of the scattered light from pure liquids. The exciting line is found, by photographic means, in the scattered light accompanied by other distinct lines on the longer wave length side. In some cases a line equally distant from the exciting line is found on the short wave length side. The interpretation of the effect is not yet sufficiently advanced to warrant discussion.

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PHOTOTROPY

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INTRODUCTION

"The first observation was that a gate post painted white by means of a new pigment having a zinc basis appeared black all day and white all night, turning black again soon after sunrise, *et ainsi de suite* for any number of days" (82).

Mr. Thomas Griffiths, F.C.S., the possessor of this remarkable gate post, very naturally exhibited it to his friend, Dr. T. L. Phipson, who had written a book on phosphorescence, and who proceeded to write about the gate post.

As a result of Dr. Phipson's writings, which appeared in 1881, the matter came to the attention of the manufacturer of the "new pigment having a zinc basis," who divulged the information that Mr. Griffith's post was not nearly so original as it was considered; that he had been familiar with this property of lithopone for ten years, and that it had caused a great deal of trouble in his business. He added that he had recently supplied Mr. Griffiths with paint that would stay unblushingly white no matter how great the illumination. As the manufacturer's note appeared in 1881 the property of lithopone to undergo a reversible color change induced by light was probably first recognized about 1870 (61).

Mr. Griffiths's gate post received a certain amount of publicity in 1881 and even as late as 1891 (12), and its peculiar behavior led Dr. Phipson to suggest that lithopone might contain a new element, for which he proposed the name "Actinium," though, unfortunately, he endowed it with properties totally different from those of the actinium of today (83). However, it was not recognized that the color change exhibited by certain samples of lithopone might be a phenomenon common to a variety of substances rather than due to the presence of a hypothetical new element, and the observation of ter Meer (117), published five years before Phipson's first paper, that the potassium salt of dinitroethane underwent the same sort of color change, remained unnoticed. Therefore, Mr. Griffiths's post continued an isolated wonder until it was forgotten.

In 1899 Marckwald (47) observed that two different organic compounds, anhydrous quinoquinoline hydrochloride and β -

tetrachloro- α -ketonaphthalene, became colored when exposed to light, and that they lost this light-induced coloration when placed in the dark. He recognized that this reversible color change characterized a new phenomenon, and considered it an instance of a truly reversible photo-reaction. He introduced the term "phototropy" to cover, apparently, reversible photo-reactions in general. The use of "phototropy" in this sense has not been retained, but it has been generally adopted to designate the phenomenon of a color change induced by light and reversing in the dark. The choice of the word is, perhaps, not happy. Not only has it been in use by biologists for many years in connection with color adaptations of living organisms but the form of the word does not suggest to the English-speaking scientists that it refers to a phenomenon rather than to a field of knowledge. However, the term has become well established.

An exact definition of phototropy as it may now be strictly considered is difficult to formulate. It is to be hoped that further investigation will make it possible to restrict the term to a fundamentally new phenomenon. Since the term "Phototropy" was first proposed investigators have felt that the reversible light-induced color changes exhibited by tetrachloro-ketonaphthylene, certain anils, hydrazones, osazones and fulgides formed a coherent group of phenomena, and might be considered truly phototropic. It is difficult, however, to find a single distinguishing characteristic in the phenomena exhibited by these substances. Perhaps the most striking feature is that these color changes are true adaptations; that high frequency light causes the substances to absorb light of longer wave length, while low frequency light, which is absorbed by the new absorption bands, causes the reverse color change. There are exceptions to this criterion, but it is the best now available. (See reference 104 for a further discussion.)

As the mechanism of the phototropic reaction shown by these substances is not clearly understood, and as it is not known in certain cases whether or not a substance is phototropic in the restricted sense referred to, the term is given a broad interpretation in this review. Reversible, light-induced color changes generally are discussed. These, whether or not they may be truly

phototropic in a strict sense, are all suggestive and of interest to anyone concerned with phototropy.

Simultaneously with Marckwald's discovery Biltz observed the phototropy of benzaldehyde-phenylhydrazone and certain osazones (6, 7, 8). It is curious to note that both Emil Fischer, who discovered benzaldehyde-phenylhydrazone (20), and Zincke, who discovered the chloronaphthalene derivative (133), observed the color change produced in these substances by light but failed to notice the reverse change which took place in the dark.²

Since these first discoveries, a great number of other phototropic substances have been found, and at the present over two hundred are known. Most of these substances are organic, although some are inorganic; and most phototropic substances exhibit phototropy only in the solid state. In the last few years a number of substances have been discovered to exhibit phototropy in solution, and with one possible exception, these compounds are not known to be phototropic in the solid phase.

There is a long known class of compounds the members of which show a color change when exposed to light and revert to their original color in the dark. These are the phosphorescent substances. As these substances absorb light they begin to reemit light. Therefore, when a phosphorescent substance is brought from the dark into the light the color of the substance changes until an equilibrium is reached between the rates of light absorption and light emission. This "saturation" of absorption bands has been known and studied for some time, but the substances themselves have never been considered as phototropic. We know very little about the relationships between the mechanisms of phosphorescence and phototropy, and therefore the exclusion of phosphorescent substances from classification as phototropic may be arbitrary and superficial. However, if only because of practical limitations of space, the present review must be limited to the behavior of phototropic substances whose color change is not due directly to the re-emission of absorbed light. As a matter of fact, both zinc sulfide and the alkaline earth sulfides do show phototropy,

² However Wislicenus noticed that the color change of benzaldehyde phenylhydrazone was reversible (*Ann.*, 277, 366 (footnote) (1893)).

but in this the color change is of the opposite sign from that caused by saturation of the phosphorescent absorption bands.

Even excluding the phosphorescent materials, phototropy remains a diversified phenomenon. It is exhibited by pure substances, by liquid and solid solutions, and possibly by mixtures. A number of theories have been advanced to account for the various manifestations of phototropy. Such a plurality of theories may be justified since it is possible that in different cases totally different mechanisms may be involved, and consequently that no general explanation could be formulated. But even the illumination afforded by the individual theories leaves certain phases of phototropy obscure, and we are in no position to start with one, or several, generalizations and derive the known facts of the phenomenon.

Therefore the following review will be divided into two parts so as to present first the experimental data, and then the theories which have been proposed to account for the observed facts.

PART I. EXPERIMENTAL OBSERVATIONS

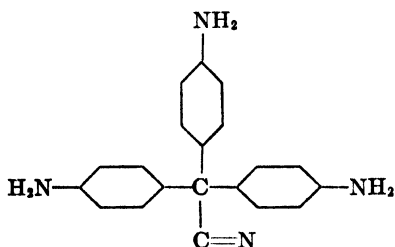
Phototropy in liquid systems

Except for non-crystalline solids, which in this review are classified as solids rather than liquids, all of the known phototropic liquids are solutions. The phototropy of these solutions is dependent on the nature of both the solute, which may be considered as carrying the phototropic properties, and on the solvent. While the color developed is apparently independent of the nature of the solvent, the intensity of the color developed is very greatly dependent on the solvent.

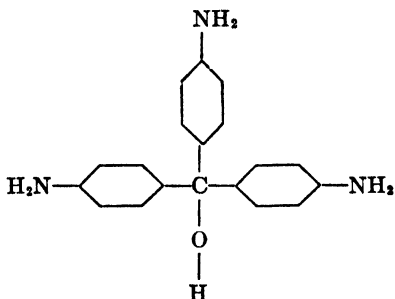
Known phototropic liquids

Dye derivatives. Most of the known phototropic liquids are solutions of colorless derivatives of basic triphenylmethane dyes. The cyanides, carbinols, and sulfites of various of these dyes have been found to be phototropic in solution. The solutions are colorless, or faintly colored, in the dark, but acquire the color of the parent dyestuff on exposure to light. The constitutions as-

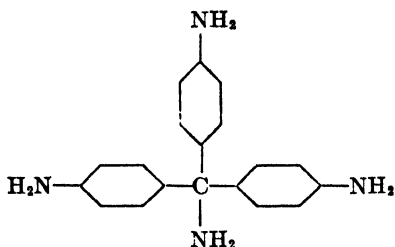
cribed to these derivatives may be exemplified by the structures of those derived from pararosaniline which are given below:



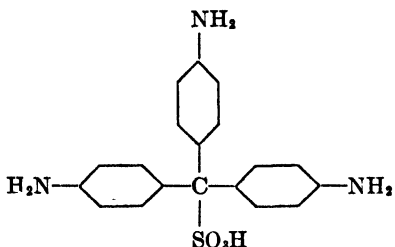
Pararosanine cyanide



Pararosanine carbinol



Pararosanine amine base (125)



Pararosanine sulfite

The formulas represent the colorless forms, and the word "leuco" is sometimes introduced into the names of these compounds, as "pararosanine *leuco* cyanide," to emphasize their colorless state. But this seems hardly necessary, since presumably the isomeric colored derivatives are not stable under ordinary conditions.

The solutions which contain dyestuff derivatives and are known to be phototropic are the following:

Cyanides:

Pararosanine cyanide
Crystal violet cyanide
Malachite green cyanide
Brilliant green cyanide
Auramine cyanide

Solvents: ethyl alcohol (42), ethyl ether, benzene (36)

Benzaurine cyanide
Phenolphthalein cyanide

Solvents: Water, or aqueous alcohol, containing KCN (43)

Carbinols:

Malachite green carbinol	} Solvents: ethyl alcohol made alkaline with KOH (42, 44); benzene (36)
Crystal violet carbinol	

Benzaurine carbinol	} Solvents: Water, or aqueous alcohol, containing KOH (43)
Phenolphthalein carbinol	

Amine Bases:

The amine base of malachite green in benzene or in ethyl alcohol containing ammonia becomes colored green under the influence of light. The amine base of crystal violet in the solvents just mentioned and in ethyl ether also becomes colored in light. From the author's description it is uncertain whether or not these solutions lose their color, or even a part of it, on standing in the dark. It is, therefore, uncertain whether they are phototropic or not (36, 43).

Sulfites:

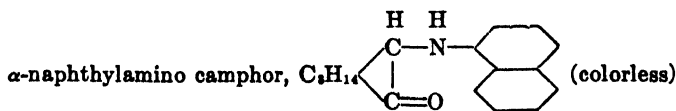
Pararosaniline hydrochloride sulfite in water containing sulfur dioxide (36, 44)
 Rosaniline sulfite in water containing sulfur dioxide (34)
 "Methyl violet" sulfite in water containing sulfur dioxide (34)
 Crystal violet sulfite in water containing sulfur dioxide (34)
 Malachite green sulfite in water containing sulfur dioxide (34)

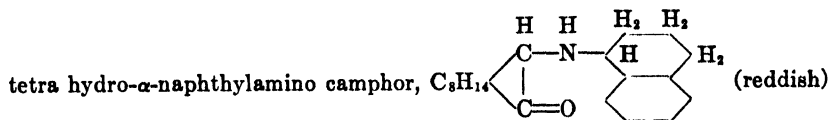
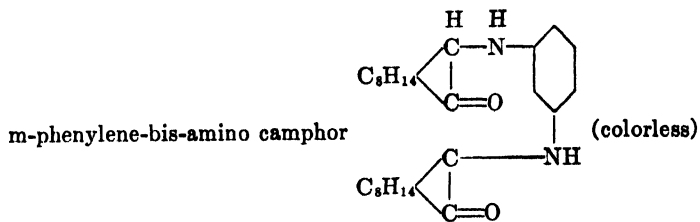
The following solutions of related substances have been examined and found to be not phototropic (36):

Sulfite of brilliant green
 Sulfite of brilliant green sulfate
 Victoria blue cyanide

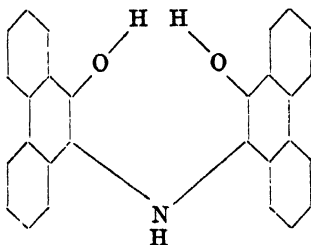
In view of later work the impossibility of obtaining phototropic solutions of brilliant green sulfite is doubtful (34, 43).

Camphor derivatives. The three substances listed below form phototropic solutions in chloroform (105). The color of the solutions in the dark is indicated for each compound. The color produced by light is green in all three cases. The compounds are:





Other solutions. 10·10'-dihydroxy-diphenanthryl-9,9'-amine,



is phototropic in ethereal solution (92). The solution is brownish red in the dark and becomes bright yellow on exposure to sunlight. This is the first instance so far mentioned in which light causes a reversible fading of color rather than a deepening of color.

A benzene solution of equal molecular proportions of diphenyl-monobiphenylmethane and diphenyl-monobiphenyl methyl chloride when placed in a sealed tube and exposed to sunlight acquires a reddish color, visually similar to the color of benzene solutions of diphenyl-monobiphenyl-methyl (91). In the dark the solution loses its reddish color, and returns to its colorless condition. Likewise a benzene solution of equivalent amounts of phenyl-dibiphenyl-methane and phenyl-dibiphenyl-methyl chloride becomes colored in the light, the color being apparently that of phenyl-diphenyl-methyl (91).

An aqueous solution of potassium ferrocyanide which contains a little phenolphthalein turns red in the light, and regains its original yellow color in the dark (4).

A solution of molybdenum trioxide in selenium oxychloride is normally light yellow but becomes indigo blue in sunlight and yellow again when placed in the dark or warmed (40).

Benzaldehyde phenylhydrazone, and probably certain others show transient phototropic properties in benzene solution when exposed to air (22). The color changes are, no doubt, intermediate stages in an irreversible oxidation (116). A similar phenomenon has long been known to take place with partially oxidized photographic developers made of ferrous oxalate.

The color change

The exciting light. The excitation of the phototropic change follows the Grotthus law (109, 110, 111, 112, 114, 128), and only light absorbed by the phototropic substance is active in producing a color change. The phototropic dye and camphor derivative solutions are colorless, or nearly so to the eye, and it is known that the exciting light is ultra-violet.

In some cases it is mentioned that the phototropic change is not produced by light transmitted by glass, while it is produced by light transmitted by quartz. Usually no direct determination of the active wave lengths has been made. The dye sulfite solutions appear to be the only ones which consistently require light of shorter wave lengths than is transmitted by glass (34).

The ultra-violet absorption spectra of some of the dye cyanide, amine base and carbinol solutions have been determined, but it is not known whether all or only a part of the absorbed wave lengths is active in producing the color change (36).

In considering the relationship between the magnitude of the color change, and the intensity of the light and the time of exposure to light it will be seen that the color change will not indefinitely increase in magnitude as the exposure is prolonged, but that an equilibrium point will be reached beyond which further exposure will not produce a further color change. There are two opposing reactions to be considered: first, the formation of color, or in a few cases, the bleaching caused by the action of light; and, second, the opposed "dark" reaction which destroys the color formed by light or restores the color destroyed by light.

Of course, this reverse reaction does not take place unless the "light" reaction has preceded it. This reverse reaction takes place in the light as well as in the dark, and, in the case of solutions, its rate does not appear to be directly influenced by the action of light.

Therefore, the speed with which the equilibrium point is reached, and the magnitude of the color change which the solution undergoes should bear some direct relation to the intensity of the light for any given frequency. That there is some such relationship seems to be the case, but the only attempt to make a quantitative examination of the relation for phototropic solutions was an approximate determination of the variation of the color produced in a rosaniline sulfite solution when the intensity of the white light employed was varied. The conclusion reached was that the intensity of the color at the stationary point was directly proportional to the intensity of the exciting white light (34).

The color produced. The color produced by the action of light on alcoholic solutions of pararosaniline cyanide was spectroscopically examined and compared with the color of pararosaniline chloride. The conclusion was reached that the two colors were identical (36, 42, 44). In the same way the colors of a light stimulated solution of rosaniline sulfite and rosaniline chloride were compared, and the conclusion was also the two colors were identical (34). There appear to have been no exact observations on the color produced by light in phototropic solutions of substances other than the dyestuff derivatives.

The intensity of color produced in solutions of dyestuff derivatives varies not only with the intensity of the exciting light, but also with the concentration of the photoactive solute and the presence or absence of other substances in solution. With rosaniline sulfite the color produced appears to be directly proportional to the concentration of the dyestuff derivative, other factors remaining constant (34). The color varies greatly with the concentration of sodium sulfite or bisulfite in the solution (34).

The addition of potassium cyanide to alcoholic solutions of the dye cyanides reduces the intensity of color which can be produced by light, and it further greatly accelerates the dark reaction so

that the fading of the color produced by light may take minutes instead of hours or weeks. Potassium hydroxide has a similar effect upon alcoholic solutions of the carbinols (36, 42, 44).

The velocity with which color is formed by the action of light on certain solutions of rosaniline sulfite has been roughly determined and plotted (34).

Working with solutions of malachite green carbinol, Ariga (2) found that the velocity of the color change was directly proportional to the intensity of the light and independent of the temperature and the concentration of alkali.

The work to be described below upon the variation of the conductivity of solutions of dye cyanides and carbinols is probably an indirect determination of the velocity of coloration.

The actual time required for the development of an appreciable color change when a phototropic solution is exposed to light varies with the solution, and, of course, with the conditions of illumination; however, it is seldom over two minutes in bright sunlight.

Phenomena accompanying the phototropic change

Optical rotation. A solution of 0.726 gram of α -naphthylamine camphor in 100 cc. of chloroform showed a specific rotation of the mercury green line 5461 A. of 126° . When exposed to sunlight for six minutes, the solution changed from colorless to deep green, and the specific rotation changed to 186.6° . When placed in the dark after this exposure, the color of the solution faded, and the angle of rotation decreased. It is said that the change in the dark required days, and as further data are not given, it seems possible that the reverse reaction was not followed through and that it is not certain that the solution reverts to its original rotation (106).

Conductivity. When phototropic solutions of dye cyanides and carbinols in alcohol are exposed to light, the conductivity of the solutions increases. When the light is shut off the conductivity falls again (36, 44). Details of typical cases of this very interesting parallelism are shown in tables 1 and 2.

The measurements shown in table 1 are on a N/1000 solution

of malachite green cyanide in absolute alcohol. The conductivity was measured at 25°. The light source was a mercury quartz

TABLE 1
Specific conductivity of malachite green cyanide (36, 44)

Original solution.....	3.5×10^{-7}
After illumination with a quartz lamp for 2 hours.....	35×10^{-7}
In the dark:	
After 2 minutes.....	31×10^{-7}
After 5 minutes.....	27×10^{-7}
After 41 minutes.....	14×10^{-7}
After 46 minutes.....	13×10^{-7}
After 51 minutes.....	12×10^{-7}
After 2 hours and 49 minutes.....	6×10^{-7}
After 2 hours and 59 minutes.....	5×10^{-7}
After 4 hours and 50 minutes.....	4×10^{-7}
After 5 hours and 0 minutes.....	4×10^{-7}
After 23 hours and 45 minutes.....	3×10^{-7}
After 51 hours and 15 minutes.....	3×10^{-7}

TABLE 2
Specific conductivity of pararosaniline cyanide (36, 44)

	$k/10^{-7}$
After illumination with an iron-nickel arc, 1 hour.....	18
After illumination with an iron-nickel arc, $1\frac{1}{2}$ hours.....	27
After illumination with an iron-nickel arc, 2 hours.....	41
In the dark after 19 hours.....	37.5
After additional illumination with the arc, 20 minutes.....	48.5
After additional illumination with the arc, 45 minutes.....	53
After additional illumination with the arc, $1\frac{1}{2}$ hours.....	72.5
In the dark for an additional 66 hours.....	51
After additional illumination for $1\frac{1}{4}$ hours.....	70.5
After additional illumination for $2\frac{1}{2}$ hours.....	100
In the dark for an additional 18 hours.....	68
After additional illumination for $\frac{3}{4}$ hour.....	82.5
After additional illumination for $3\frac{1}{4}$ hours.....	86.5
After additional illumination for $4\frac{1}{2}$ hours.....	91
After an additional 106 days in the dark.....	52.5

lamp, and the temperature of the solution was 12° during the illumination.

In table 2 are shown the conductivities at 25° of a N/1000 solution of a pararosaniline cyanide in absolute alcohol. The light source was an iron-nickel arc, and the temperature of the solution during the exposure to light was 12°.

The conductivity of alcohol used as the solvent was 3×10^{-7} to 7×10^{-7} .

The figures given for malachite green cyanide are all that could be desired for a reversible reaction, and similar results were obtained for brilliant green cyanide. The data on the carbinols of malachite green and crystal violet are not so conclusive since the conductivities of their solutions increased on merely standing in the dark, but it would seem that the high conductivity produced by light was completely lost on standing in the dark.

With the pararosaniline cyanide it will be noticed that the specific conductivity after exposure to light never reverts to anything like its original value. The same is true of the specific conductivities of the solutions of the cyanides of crystal violet and auramine. The alcoholic solution of victoria blue cyanide, which becomes colored in the light but does not fade in the dark, shows a specific conductivity which steadily increases with the exposure to light, and shows no falling off when the solution is placed in the dark.

Fatigue. The ethereal solution of 10,10'-dihydroxy-diphenanthryl-9,9'-amine after long exposure to sunlight remains bright yellow and will no longer become brownish red in the dark (92). There are no further data to show the nature of the change which has taken place. For want of further information we may refer to it as "fatigue."

An alcoholic solution of pararosaniline cyanide which contains potassium cyanide shows a somewhat similar behavior. Such a solution contained in a sealed tube becomes brownish and loses its phototropic properties when exposed to daylight, even in Chicago, for a few weeks.

On the other hand, the selenium oxychloride solution of molybdenum trioxide is very stable to light, and sealed tubes of this solution have been exposed to light for over eight years without diminution of the power to change color (49).

The phototropy of solids

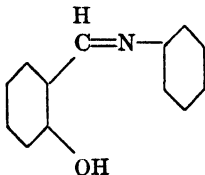
Most of the work which has been done upon phototropy concerns solid systems, and has been largely devoted to a search for phototropic substances. This search has been carried on primarily by four groups of scientists; Padoa and his collaborators in Italy; Senier and his pupils in England; Stobbe in Germany; and Mourelo in Spain. In recent years a number of phototropic substances have been discovered in India. Isolated discoveries of phototropic substances have been made by other workers. Critical investigations of the phenomenon itself have been carried on especially by Chattaway, Padoa, Stobbe, and Weigert.

The known phototropic solids

In this section will first be listed the known phototropic organic compounds; then the inorganic systems.

There is a dearth of quantitative information on the rate with which phototropic solids undergo their color changes. But for the benefit of those who have not had practical experience in this field, it may be said that the time required for bright sunlight to produce a pronounced color change is of the order of from a few seconds to many minutes. The reverse change in the dark at room temperature requires from a minute or two to several weeks.

Anils. The condensation products of aldehydes and primary amines, which are variously known as Schiff bases or anils, have the general formula, $R - CH = N - R'$; in which R and R' are organic radicals. A typical anil is salicylidene aniline, whose formula is given below:



About 275 anils have been examined for phototropy, and some twenty-two have been found to be phototropic. The phototropic anils are colorless or light yellow when unaffected by light, and red or brownish red in sunlight.

TABLE 3
The phototropic anils

AMINES	ALDEHYDES			
	Salicylaldehyde	o-Nitro-benzaldehyde	p-Hydroxy-benzaldehyde	2-Hydroxy-3-methoxy-benzaldehyde
		(96)	(97)	(103)
Aniline	+ (101)	—	—	—
o-Toluidine	—	—	—	—
m-Toluidine	+ (101)	—	—	—
p-Toluidine	—	—	—	—
o-Chloroaniline	+ (102)	+	—	—
m-Chloroaniline	— (102)	+	—	—
p-Chloroaniline	— (102)	—	—	—
o-Bromoaniline	+ (81)	—	—	—
m-Bromoaniline	+ (103)	—	—	—
p-Bromoaniline	+ (81)	—	+	—
o-Phenylenediamine	— (103)†	†	—	—
m-Phenylenediamine	+ (103)	—	—	—
p-Phenylenediamine	— (102)	—	—	—
m-Aminophenol	— (102)	—	—	—
o-Anisidine	+ (103)	—	+	—
m-Anisidine	— (103)	—	—	—
p-Anisidine	+ (103)*	—	—	—
p-Phenetidine	— (24)	—	—	—
p-Aminobenzaldehyde	— (24)	—	—	—
o-Aminobenzoic acid	— (24)	—	—	—
m-Aminobenzoic acid	+ (81)§	—	—	—
p-Aminobenzoic acid	+ (102)	—	—	—
p-Amino-methylbenzoate	— (24)	—	—	—
p-Amino-ethylbenzoate	+ (24)	—	—	—
o-Aminocinnamic acid	+ (24)	—	—	—
Xylidine (NH ₂ :CH ₃ :CH ₃ ::1:2:4)	— (101)	+	+	—
Xylidine (NH ₂ :CH ₃ :CH ₃ ::1:2:5)	— (101)	—	—	+
Xylidine (NH ₂ :CH ₃ :CH ₃ ::1:3:4)	+ (102)	—	—	—
Xylidine (NH ₂ :CH ₃ :CH ₃ ::1:3:5)	— (102)	—	—	—

* Phototropic only at low temperatures.

† Monosalicylidene-o-phenylene diamine is phototropic at low temperatures (24).

‡ The monosalicylidene compound is not phototropic. The disalicylidene compound has not been investigated.

§ Gallagher reports that this is not phototropic (24), but Stobbe made some quantitative measurements of its phototropic properties.

TABLE 3—Continued

AMINES	ALDEHYDES			
	Salicylaldehyde	o-Nitro-benzaldehyde	p-Hydroxy-benzaldehyde	2-Hydroxy-3-methoxy-benzaldehyde
		(96)	(97)	(103)
4-Cumidine.....	— (101)	—		
Mesidine.....	— (102)			
m-Nitroaniline.....	— (24)			
p-Nitroaniline.....	— (24)			
Nitro- ψ -cumidine.....	— (24)			
α -Naphthylamine.....	— (101)	—	—	
β -Naphthylamine.....	+ (102)	—	—	—
α -Chloro- β -naphthylamine.....	— (24)			
1:2-Naphthalene diamine.....	— (24) ¶			
1:4-Naphthalene diamine.....	— (24)			
1:5-Naphthalene diamine.....	— (24)			
1:8-Naphthalene diamine.....	— (24)			
2:7-Naphthalene diamine.....	— (24)			
Benzidine.....	— (24)	—		
4,4'-Diamino-2,2'-dimethyldiphenyl.....	— (24)			

¶ The monosalicylidene compound is not phototropic either (24).

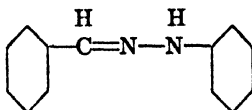
In table 3 are listed all of the known phototropic anils. In this table the anils are indicated by the aldehyde and primary amine from which they are formed. It will be seen that all the phototropic anils are derived from four aldehydes; salicylaldehyde, o-nitro-benzaldehyde, p-hydroxybenzaldehyde, and 2-hydroxy-3-methoxy-benzaldehyde. With the exception of a few salicylaldehyde derivatives described by Gallagher (24) this table lists not only the phototropic anils but all of the anils derived from the four aldehydes which have been studied for phototropy.

In the table a plus sign means that the anil is phototropic, a minus sign that it is not phototropic. A blank space indicates that the anil has not been examined for phototropy. The numbers in brackets indicate the references in which the anils are described. When an anil is derived from a diamine, the data

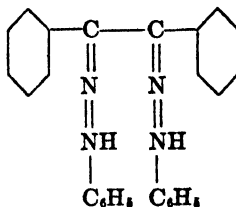
given in the table refer to the anil formed by the condensation of one molecule of diamine and two molecules of aldehyde. If the anil formed by the condensation of one molecule of a diamine with one molecule of an aldehyde has been studied, it is referred to in the footnotes.

In addition to the substances listed in the table a number of anils derived from benzaldehyde, cinnamic aldehyde, m-nitrobenzaldehyde, p-nitrobenzaldehyde, m-hydroxybenzaldehyde, o-methoxybenzaldehyde, anisaldehyde, 2-hydroxy-5-methyl benzaldehyde, 2-hydroxy-m-tolylaldehyde, 6-hydroxy-m-tolylaldehyde, 2-hydroxy-5-bromo-benzaldehyde, 2-hydroxy-3-nitro benzaldehyde, 2,4-dihydroxy-benzaldehyde, vanillin, piperonal, and 2-hydroxy-naphthaldehyde-1, have been prepared and examined for phototropy. A list of these is given in reference No. 114.

Hydrazones and osazones. A number of phototropic hydrazones derived from aromatic hydrazines are known, as are also certain osazones derived from aromatic alpha diketones. The general structure of the hydrazones may be exemplified by benzaldehyde phenylhydrazone:



Benzil phenyl osazone shows the typical osazone structure:



In table 4 are listed all the known phototropic hydrazones and osazones. As with the anils, the data given refer to the hydrazone or osazone formed by the condensation of the hydrazine named over the datum with the aldehyde, ester, or α -diketone named at the side. In listing the hydrazines only the

TABLE 4
The phototropic hydrazones and osazones

[illegible]

ORASONES														
	(7)	(74, 75)	(75)	(74, 75)						(66)	(66)	(66)	(76)	(76)
Benzil.....	+	+ β	+ β	+ β										
Cuminil.....	+ β	+ β	+ β	+ β										
Anisil.....	+	- β	+ β	+ β						+	+	-	-	-
Piperil.....	+	+	+	+ β						+	+	+	+	+

distinctive part of the name of the hydrazine is given. Thus, "phenyl" represents phenylhydrazine; "o-Tolyl" represents o-Tolylhydrazine; "Diphenyl" stands for Diphenylhydrazine, and so on. In the case of each aldehyde, ester, and diketone named in this table every hydrazine derivative which has been specifically studied for phototropy is listed whether it is phototropic or not.

The osazones occur in stereoisomeric forms. Both forms of the phenyl osazones of benzil, anisil, and piperil have been studied for phototropy, and found to be phototropic. Only one modification of the other osazones has been studied. When the classification of this modification has been noted in the literature this is indicated by the letter β , since all listed osazones that have been identified, with the exception of the three forms just referred to, are designated as β .

The positive and negative signs and blank spaces have the same significance as in table 3.

In addition to the compounds listed in table 4 the following hydrazones and osazones have been examined for phototropy and found not to be phototropic:

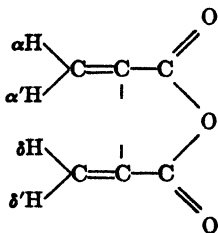
The β -naphthylhydrazones of acetaldehyde, phenyl-acetaldehyde, propionaldehyde, n-butylaldehyde, iso-valerylaldehyde, galactose, glucose, acetone, o-nitrobenzaldehyde, m-nitrobenzaldehyde, and p-nitrobenzaldehyde (118)

The phenylhydrazone, p-tolylhydrazone, β -naphthyl-hydrazone, and diphenylhydrazone of acetaphenone (10)

The α and β forms of salicyl-phenylosazone (7)

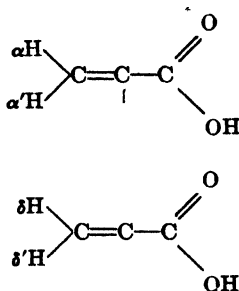
Of the two hundred odd hydrazones and osazones which have been investigated 57 hydrazones and 20 osazones (not counting the stereoisomers as individuals) have been found to be phototropic.

Fulgides. Stobbe has investigated a whole series of compounds some of which he discovered to be phototropic (109), and of which the parent substances are called "fulgides" and are considered to be derived from the acid anhydrid



by substitution of the lettered hydrogen atoms.

Corresponding to the fulgides proper, i.e., the substituted acid anhydrides, there can also be prepared the free acids, derived from,



and also salts and esters of the acids.

Belonging to this series there are, then, the fulgides, the fulgic acids, the salts of the acids and the esters of the acids. As there are in the parent substance four hydrogen atoms which may be substituted by organic radicals, and as all fulgides may exhibit cis-trans isomerism it will be seen that the possible derivatives of the parent substance are innumerable. Consider for a moment the fulgide series which may be obtained by the use of only the phenyl group as substituent. There could be one monophenylfulgide, two diphenyl fulgides, one triphenyl and one tetraphenyl fulgide, making four in all, not counting the stereoisomers. From each fulgide a fulgic acid may be obtained, and from each fulgic acid a series of salts and esters, and mixed esters and salts. Moreover, even the neutral sodium salt of a given fulgic acid may or may not be phototropic depending on whether or not the salt is anhydrous or contains water of crystallization.

TABLE 5

The phototropic fulgides

α -phenyl- δ δ' -dimethyl fulgide.....	—
Allo- α -phenyl- δ δ' -dimethyl fulgide.....	—
α -Phenyl- α' δ δ' -trimethyl fulgide.....	—
Allo- α -phenyl- α' δ δ' -trimethyl fulgide.....	—
α -(p-Tolyl)- δ δ' -dimethyl fulgide.....	—
α -Cumyl- δ δ' -dimethyl fulgide.....	—
α -(o-Nitrophenyl)- δ δ' -dimethyl fulgide.....	—
α -(m-Nitrophenyl)- δ δ' -dimethyl fulgide.....	—
α -(p-Nitrophenyl)- δ δ' -dimethyl fulgide.....	—
α -(o-Methoxyphenyl)- δ δ' -dimethyl fulgide.....	—
α -Anisyl- δ δ' -dimethyl fulgide.....	—
α -Veratryl- δ δ' -dimethyl fulgide.....	—
α -Piperonyl- δ δ' -dimethyl fulgide.....	+
α - δ -Diphenyl fulgide.....	+
α - δ -Diphenyl- δ δ' -dimethyl fulgide.....	+
α α' -Diphenyl- δ δ' -dimethyl fulgide.....	+
α -Anisyl- δ -phenyl fulgide.....	+
α -Piperonyl- δ -phenyl fulgide.....	+
α -Piperonyl- δ -phenyl- δ' -methyl fulgide.....	—
α -Piperonyl- δ -naphthyl- δ' -methyl fulgide.....	—
α - δ -Dicumyl fulgide.....	+
α δ -Dicumyl isofulgide.....	+
α δ -dianisyl fulgide.....	+
α δ -diveratryl fulgide.....	+
α δ -dipiperonyl fulgide.....	—
Allo- α δ -dipiperonyl fulgide.....	—
α δ δ' -triphenyl fulgide.....	+
α -(p-Tolyl)- δ δ' -diphenyl fulgide.....	+
α -Cumyl- δ δ' -diphenyl fulgide.....	+
α -(p-Chlorophenyl)- δ δ' -diphenyl fulgide.....	+
α -(o-Nitrophenyl)- δ δ' -diphenyl fulgide + 1 $\frac{1}{2}$ CHCl ₃	+
α -(m-Nitrophenyl)- δ δ' -diphenyl fulgide.....	—
α -(p-Nitrophenyl)- δ δ' -diphenyl fulgide.....	+
α -(o-Methoxyphenyl)- δ δ' -diphenyl fulgide.....	+
α -(p-Methoxyphenyl)- δ δ' -diphenyl fulgide.....	+
α -(o-Ethoxyphenyl)- δ δ' -diphenylfulgide.....	+
α -Anisyl- δ δ' -diphenyl fulgide.....	—
α -Veratryl- δ δ' -diphenyl fulgide.....	+
α -Piperonyl- δ δ' -diphenyl fulgide.....	—
α -Piperonyl- δ δ' -diphenyl-allo-fulgide.....	+
Tetraphenyl fulgide.....	+
Tetraphenyl-allo-fulgide.....	+

TABLE 5—Continued

The phototropic fulgides—Continued

α -Styryl- δ δ' -dimethyl fulgide.....	—
α δ -Distyryl fulgide.....	+
α -Styryl- δ δ' -diphenyl fulgide.....	+
α -Furyl- δ δ' -dimethyl fulgide.....	—
α - δ -Difuryl fulgide.....	+
α -Furyl- δ δ' -diphenyl fulgide.....	+
α -Diphenylene- δ δ' -dimethyl fulgide.	
α -Diphenylene- δ -phenyl fulgide.....	
α -Diphenylene- δ δ' -diphenyl fulgide.	

Fulgic acids, salts and esters

α -Phenyl- δ δ' -dimethyl-allo-fulgic acid.....	
α -Phenyl- α' δ δ' -trimethyl fulgic acid.	
α (p-Tolyl)- δ δ' -dimethyl fulgic acid.....	—
α -(o-Nitrophenyl)- δ δ' -dimethyl fulgic acid.....	—
α -(m-Nitrophenyl)- δ δ' -dimethyl fulgic acid.....	—
α -(p-Nitrophenyl) δ δ' -dimethyl fulgic acid.....	—
α -(o-Methoxyphenyl)- δ δ' -dimethyl fulgic acid.....	—
α -Anisyl δ δ' -dimethyl fulgic acid.....	—
α -Veratryl- δ δ' -dimethyl fulgic acid.....	—
α -Piperonyl- δ δ' -dimethyl fulgic acid.....	—
α δ -Diphenyl fulgic acid.....	+
Ester.....	—
Sodium salt + 1 H ₂ O.....	+
Sodium salt anhydrous.....	—
α δ -diphenyl- δ' -methyl fulgic acid.....	—
α α' -Diphenyl- δ δ' -dimethyl fulgic acid.....	—
α -Anisyl- δ -phenyl fulgic acid.....	
Sodium salt.....	—
Barium salt.....	—
α -Veratryl- δ -phenyl fulgic acid.....	—
α -Piperonyl- δ -phenyl fulgic acid barium salt.....	—
α - δ -Dianisyl fulgic acid sodium salt.....	—
α δ -Diveratryl fulgic acid.....	+
α δ -Dipiperonyl fulgic acid.....	
Potassium salt.....	—
Ester.....	—
α δ -Dipiperonyl-allo-fulgic acid potassium salt.....	+
α δ -Triphenyl fulgic acid.....	+
Sodium salt.....	+
Calcium salt.....	+
Barium salt.....	—
Piperidine salt.....	—

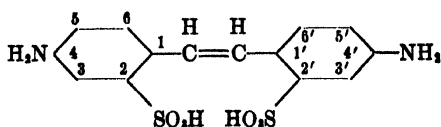
TABLE 5—Continued

<i>Fulgic acids, salts and esters—Continued</i>	
α -(p-Tolyl)- δ δ' -diphenyl fulgic acid.....	+
Sodium salt.....	+
α -Cumyl- δ δ' -diphenyl fulgic acid.....	—
Sodium salt.....	+
Barium salt.....	+
α -(p-Chlorophenyl)- δ δ' -diphenyl fulgic acid.....	+
Acid ester sodium salt.....	+
α -(o-Nitrophenyl)- δ δ' -diphenyl fulgic acid.....	+
Sodium salt.....	+
α -(p-Nitrophenyl)- δ δ' -diphenyl fulgic acid.....	+
Sodium salt.....	+
α -(o-Methoxyphenyl)- δ δ' -diphenyl fulgic acid.....	+
Sodium salt.....	+
Methyl ester.....	+
α -(o-Ethoxyphenyl)- δ δ' -diphenyl fulgic acid.....	—
α -Anisyl- δ δ' -diphenyl fulgic acid.....	+
α -Veratryl- δ δ' -diphenyl fulgic acid.....	+
Potassium salt.....	—
Sodium salt.....	+
Barium salt.....	—
α -Piperonyl- δ δ' -diphenyl fulgic acid.....	—
Sodium salt.....	—
Barium salt.....	—
α -Piperonyl- δ δ' -diphenyl-allo-fulgic acid.....	—

These considerations may suggest the impossibility of preparing, at least at the present, such a simple graphic table for the fulgide series as was used for the anils and hydrazones to show the relationship, or lack of it, between the occurrence of phototropy and chemical constitution. Therefore the fulgides, fulgic acids, salts and esters are merely listed in table 5 as given by Stobbe (111, 113, 114). A positive sign after the name of a substance indicates that it is phototropic; a negative sign that it is not phototropic.

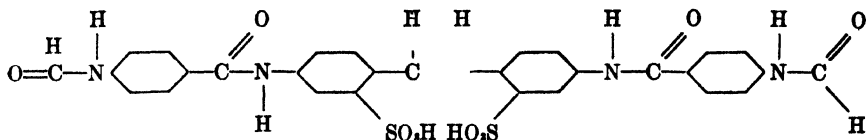
Of the 52 fulgides investigated 28 are phototropic. Of the 55 fulgic acids and their derivatives 23 are phototropic. The fulgides have initially a yellow to a red color, and the effect of light is to darken the color of the phototropic examples. The fulgic acids and their derivatives are pure white, or at most light yellow, and Stobbe suggests that some of these which he lists as not phototropic may show a change of absorption in the ultra-violet.

Stilbene derivatives (115). The dyestuff intermediate, 4,4'-diamino-stilbene-2,2'-disulfonic acid,

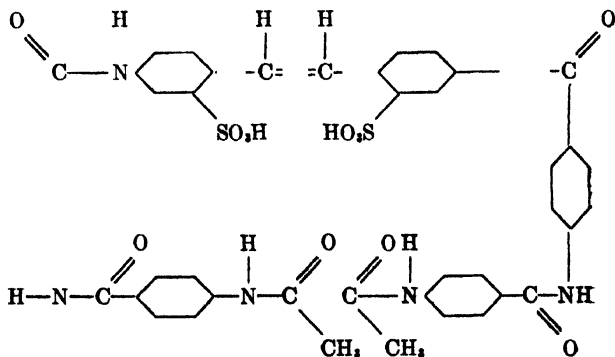


is not itself phototropic, but it is the parent substance of a series of phototropic derivatives. The five known phototropic substances of this series are derived from the original amino stilbene acid by substituting the group $-\text{COR}$ for one of the hydrogen atoms on each side of the amino groups. These all change from colorless or yellow in the dark to pink in the light and back again in the dark. The known phototropic acids obtained in this way are:

- (1) Diformyl-4,4'-diamino stilbene-2,2'-disulfonic acid;
- (2) Diacetyl-4,4'-diamino stilbene-2,2'-disulfonic acid;
- (3) Diformyl-p,p'-diamino-dibenzoyl-4,4'-diaminostilbene-2,2'-disulfonic acid, i.e.,



- (4) Diacetyl-p,p'-diamino-dibenzoyl-4,4'-diaminostilbene-2,2'-disulfonic acid;
- (5) Diacetyl-p,p'-diamino-dibenzoyl-p,p'-diamino-dibenzoyl-4,4'-diamino stilbene-2,2'-disulfonic acid, i.e.,

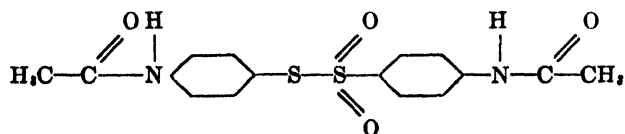


Certain salts of these acids are phototropic as well as the acids themselves. The sodium, potassium, barium, strontium, calcium, magnesium, and lead salts of the diacetyl-diaminostilbene-disulfonic acid are all phototropic.

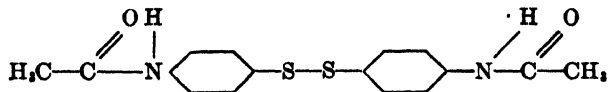
The following stilbene derivatives have been examined and found to be devoid of phototropic properties: Stilbene; stilbene-2, 2'-disulfonic acid; 4,4'-dinitrostilbene; 4,4'-dinitrostilbene; 4,4'-dinitrostilbene-2,2'-disulfonic acid; 4,4'-dichlorostilbene-2, 2'-disulfonic acid; 4,4'-diaminostilbene; diacetyl-4,4'-diaminostilbene; diformyl-4,4'-diaminostilbene; 4,4'-diaminostilbene-2,2'-disulfonic acid; dibenzoyl-4,4'-diaminostilbene-2,2'-disulfonic acid; di-p-nitrobenzoyl-4,4'-diaminostilbene-2,2'-disulfonic acid; di-p-aminobenzoyl-4,4'-diaminostilbene-2,2'-disulfonic acid; di(p-aminobenzoyl-p-aminobenzoyl)-4,4',-diaminostilbene-2,2'-disulfonic acid.

It should be noted that there exists also a non-phototropic variety of diacetyl-4,4'-diaminostilbene-2,2'-disulfonic acid (19).

Disulfoxides. Acetanilide-p-disulfoxide,



is phototropic (5) when mixed with a small quantity, about 0.1 of 1 per cent acetanilide-p-disulfide (15).



Perfectly pure acetanilide-p-disulfoxide is not phototropic, and neither is its mixture with a greater amount, 5 per cent of the disulfide (15). The disulfide must be in solid solution in the crystals of the disulfoxide in order to confer phototropic properties—simple mechanical mixture is not sufficient—and, as just mentioned, the disulfide must be present in proper concentration. Other phenyl disulfides containing amino groups, or substituted amino groups, para to the sulfur atoms may replace the acetani-

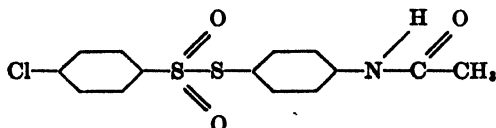
lide disulfide. However, ortho and meta compounds do not exhibit phototropic properties (15).

The following substances, which are probably in reality two component systems like the disulfoxide-disulfide combination just discussed, are also phototropic (15).

1-acetylaminonaphthyl-4-disulfoxide

2-acetylaminotolyl-5-disulfoxide

4-acetylaminophenyl-p-chlorobenzenethiosulfonate, i.e.,



The following related substances are not phototropic:

Aniline-p-disulfoxide (5)

Benzanilide-p-disulfoxide (5)

3-acetylaminotolyl-6-disulfoxide (5)

1-hydroxy-2-carboxy-phenyl-4 desulfoxide (5)

Acetanilide-p-disulfone (15)

p-tolyl-p-acetylaminobenzene thiosulfonate (15)

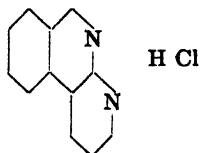
p-acetylaminophenyl-p-acetylaminobenzene sulfonate (15)

A number of corresponding compounds in which the amino groups were ortho or meta to the sulfur atoms were also prepared but were found to be devoid of phototropic properties (15).

With all of the phototropic compounds of this class exposure to light causes the color of the substances to darken. With acetanilide-p-disulfoxide the change is from colorless to yellow. The reverse change takes place in the dark.

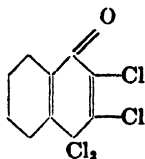
Other solid organic compounds. In addition to the classes of phototropic organic substances which have been enumerated there are scattered instances of phototropy among other widely differing organic substances.

Anhydrous quinoquinoline hydrochloride,

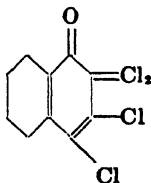


is phototropic (47). This salt turns green in light. A hydrated form of this salt containing 2 molecules of water (48) and various other quinoquinoline salts are known but are not phototropic (47).

β -tetrachloro- α -ketonaphthalene is phototropic and turns from colorless to a reddish violet in the light and back again in the dark (47). The substance has the formula,



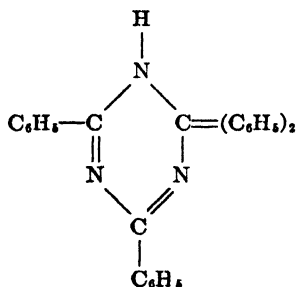
or



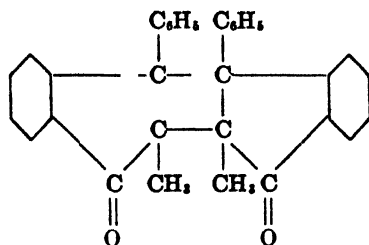
Zincke prepared two different tetrachloro-ketonaphthalenes (133), but only one of these is phototropic (128). If the phototropic variety is melted and then cooled, it is no longer phototropic, but it becomes phototropic again if inoculated with some of the original phototropic material (47, 128).

The potassium salt of dinitroethane is phototropic (13, 30, 117) and changes from yellow to reddish brown in the light and back again in the dark.

Tetraphenyl-dihydrotriazine changes from white to rose in the light, and back again in the dark (126). It apparently has the structure,



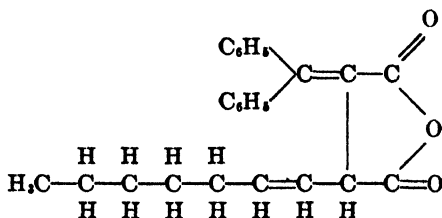
Dimethyl-diphenyl truxone,



changes from colorless to yellow in sunlight and back again in the dark (16A).

Hexanitro-diphenylamine is phototropic changing bright yellow to brown. It is remarkable for the rapidity of the color changes (114).

α, α -diphenyl- α, δ -decadiene- β, γ -dicarbonic acid anhydride,



is phototropic, showing a reversible change from yellow green to rose (93). It will be seen that this substance is somewhat similar to the fulgides.

Dibenzylamine-benzil is phototropic (62).

Colorless, solid, alkali containing benzaurine cyanide becomes violet red in sunlight (43).

A film of gelatin stained with methylene blue when exposed (in air) to the light from a Nernst lamp is bleached. If left some days in the dark the blue color returns (39).

Semicarbazones. Cinnamic aldehyde semicarbazone is white when freshly prepared, and its color does not change if the compound is stored in the dark or exposed to light. However, if the substance is exposed to sunlight for an hour and then placed in the dark the compound becomes yellow. If the substance

is again exposed to light, the yellow color disappears and the colorless modification so formed will again become yellow if placed in the dark (131). If either the yellow or colorless form is re-crystallized the original colorless form which needs to be exposed to light before it acquires phototropic properties is obtained (131). The relationships may be schematically represented as in figure 1.

In addition to cinnamic aldehyde semicarbazone the semicarbazones of o-methoxy-cinnamic aldehyde, of m-methoxy-cinnamic aldehyde, and of p-methoxy-cinnamic aldehyde, and the phenylsemicarbazones of o-methoxy-cinnamic aldehyde and p-

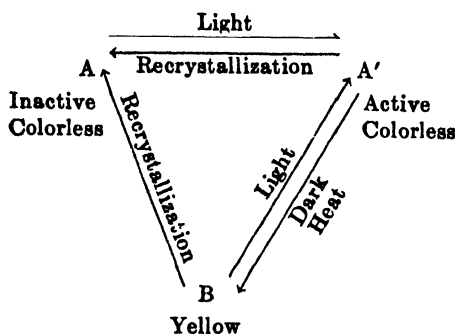


FIG. 1

methoxy-cinnamic aldehyde all exhibit this peculiar behavior to light (33). O-methoxy-cinnamic aldehyde thiosemicarbazone and m-methoxy-cinnamic aldehyde phenylsemicarbazone do not show these changes (33).

Inorganic substances

Cuprous chloride and cuprous bromide when under water containing sulfur dioxide, darken in the sunlight and regain their original colorless state when placed in the dark (107).

Lithium imide is phototropic, changing from colorless to brown (16).

Bismuth oxalate is probably phototropic (88A).

Certain samples of strontium platincyanide show a reversible color change when stimulated by x-rays (38).

Mercury compounds. In the last ten years a number of phototropic complex mercuric salts have been reported by Indian chemists. The substances of this class which have been described as phototropic are:—

1. Diiodide-dimercuric-disulfide, $I-Hg-S-S-Hg-I$ (85)
2. $HgI_2 \cdot 2HgS$ (17, 121)
3. $HgBr_2 \cdot 2HgS$ (17, 121)
4. $ClHgSCN$ (84)
5. $BrHgSCN$ (84)
6. $IHgSCN$ (84, 123)
7. $ClHgBr$ (84)
8. $ClHgI$ (84)
9. $BrHgI$ (84)
10. A compound to which is ascribed the formula $HSHgSCN$ (122, 123)

The dark stable forms of these substances vary in color from pale yellow to red. In the light they turn brown or black, and revert to their original color in the dark or on warming. The magnitude of the color change varies greatly with the different substances. Nos. 2, 6, and 10 probably show the greatest change in color, and as they become black in the sunlight their color change is more pronounced than with any organic compound.

The mixture of mercurous and silver iodides produced by toning photographic images of silver with mercuric iodide is phototropic (23). The images darken on exposure to light and regain their original reddish color on storage in the dark.

Alkaline earth sulfides. Mourelo has for many years investigated a series of phototropic alkaline earth sulfides (51, 52, 53, 54, 55, 56, 57, 58, 59). He has come to the conclusion that the pure alkaline earth sulfides are not phototropic, but that the phototropic substances are solid solutions of traces of activating elements, such as manganese and zinc, in the alkaline earth sulfides (55, 56). His published experiments, however, do not seem to establish this point beyond question.

An example of this type of phototropic substance may be prepared by the addition of 0.05 gram of sodium chloride, 0.15

gram of sodium carbonate, 0.001 gram of manganese in the form of a soluble salt, and excess of flowers of sulfur to 100 grams of strontium carbonate precipitated from strontium nitrate with sodium carbonate. The mixture is placed in a clay crucible and heated to bright redness for 4 hours. The product is greyish and becomes greenish on exposure to light (56).

The close similarity between the composition and methods of preparation of these substances, and phosphorescent sulfides and their preparation is apparent. However the phototropic properties do not appear to be due to the reemission of absorbed light, since some of the phototropic specimens, for instance the one described above, are not phosphorescent, while some of the phosphorescent products are listed as not phototropic. Moreover these compounds become darker colored in light instead of brighter.

The calcium sulfide series (55) and the strontium sulfide series (56) have been rather fully investigated.

Zinc sulfide. The malady which afflicted Mr. Griffiths's gate post has dogged the steps of the lithopone manufacturers, and, relating as it does to a commonly used substance, has been the subject of much investigation and speculation (11, 12, 18, 32, 41, 45, 46, 60, 61, 82, 89, 90, 130). Not only is lithopone itself phototropic, but pure zinc sulfide is phototropic, and the phototropic properties of lithopone are dependent upon the presence of the zinc sulfide (11, 12, 41, 60).

Hydrated, i.e., unignited zinc sulfide is not ordinarily light sensitive. If, however, the unignited zinc sulfide is boiled with a solution containing zinc ions it becomes phototropic, and retains its phototropic properties even after it has been washed as free as possible from soluble zinc salts (60, 130).

Ordinarily, however, zinc sulfide becomes phototropic only after having been heated. This effect of heating seems to be dependent upon the conversion of the zinc sulfide crystals, which are originally in the form of zinc blende, into the Wurtzite modification (89). The ignited zinc sulfide is photosensitive only when moist, and its sensitiveness is greatly increased if it is moistened with a zinc sulfate solution instead of pure water

(12). Ammonia, and formaldehyde also increase the sensitiveness (41). Lithopone suspended in celluloid is very sensitive (18).

It is only natural that the phototropy of ignited zinc sulfide should have been observed in the investigation of phosphorescent materials independently of the observations upon lithopone. Hauser (32) seems to have been the first to note the phototropy of specimens of phosphorescent zinc sulfide, although lithopone itself is also phosphorescent (11). Lenard (41) has investigated at some length the phototropic behavior of certain zinc sulfide phosphors. His results are quite consistent with those obtained by the lithopone investigators. There seems to be no direct connection between the phototropy and phosphorescence of zinc sulfide (41, 90).

Zinc oxide is not phototropic (41).

The color change

The general nature of the color changes exhibited by the various classes of phototropic substances has already been mentioned in enumerating the phototropic compounds. In many cases the mere fact that a substance changes, from, say, yellow to red, is all that is known about its color change.

In β -tetrachloro- α -ketonaphthalene (47), the fulgides (109, 111), the hydrazones and osazones (67), and the anils, the phototropic change manifests itself in an increased pleochroism of the crystals. When individual crystals of these phototropic substances are examined it is observed that the color produced by light is much more pronounced when the crystal is looked through in one direction than when it is viewed from other directions. However, some color change is observable from all sides of the crystal (128).

The color change is not uniform throughout the crystal but takes place only where the light has acted (41, 111).

Neither the fulgides (111), the anils (103), nor β -tetrachloro- α -ketonaphthalene (128) show any distortion of their crystalline form when exposed to the light, i.e., the color change is not accompanied by a distortion of the crystal.

If a phototropic compound which has been colored by exposure

to light is dissolved, the color immediately vanishes and the solution obtained appears to be identical with that prepared from the original compound which had not been exposed to light, and the solutions are not phototropic (14, 47, 101, 111).

When β -tetrachloro- α -ketonaphthalene is exposed to light it develops a new absorption band in the green. This change is not due to the shift of an ultraviolet absorption band into the visible spectrum (128).

Padoa and his collaborators made careful investigations of the velocity with which the color changes occurred in certain compounds. Their method was to prepare color standards for comparison by mixing known quantities of the weakly colored and strongly colored varieties of a phototropic substance. These standards contain a known "amount of color." The substance to be investigated is then exposed to light and the formation of color followed by comparison with these standards. The dark reaction was followed in the same way. The reaction rates obtained were found to agree to give constant velocity constants for a first or second order reaction, depending on the substance and whether the reaction was incited by light, or was the dark reaction. In some cases the light reaction is of the second order and the dark reaction of first order; in other cases the reverse is true. With salicylidene- β -naphthylamine and benzaldehyde phenylhydrazone the reaction which took place in the light was found to be monomolecular, and that which took place in the dark, bimolecular (73).

Diacetyl-4, 4'-diaminostilbene-2, 2'-disulfonic acid colors in light at the rate corresponding to a bimolecular reaction, and in the dark the reaction is monomolecular. The velocity constants vary with the intensity of the light, but neither variation in the intensity of the light nor in the wave length of the light has any influence upon the order of the reaction with the anil, the hydrazone or the stilbene compound (79).

The exciting light. In general it is known that the light which causes the phototropic change is of relatively short wave length, and lies in the blue, violet and ultraviolet regions. In one case, strontium platinocyanide, x-rays are active (38). However,

x-rays have no effect upon the organic phototropic compounds (14, 47).

The spectral sensitiveness of zinc sulfide (11, 41), β -tetrachloro- α -ketonaphthalene (111, 128), the fulgides (111), cinnamic aldehyde semicarbazone (33), and certain hydrazones, osazones, anils, and stilbene derivatives (79, 80, 111, 114, 115), has been investigated.

Solutions of β -tetrachloro- α -ketonaphthalene show the same absorption bands as the solid material which has not been excited by light (128). The absorption spectra of solutions of the fulgides (113) and of cinnamic aldehyde semicarbazone (33), have also been investigated.

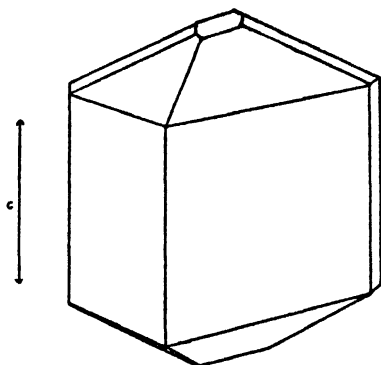


FIG. 2

The magnitude of the color change produced in β -tetrachloro- α -ketonaphthalene depends not only on the intensity of the light but also on the direction from which the light shines upon the crystal (128). This is due to the fact that light of wave lengths which are absorbed by the phototropically induced absorption band has the effect of causing this absorption band to disappear (111); and that the crystals are pleochroic.

The relationships may be made clearer by the reference to figure 2. This shows the crystal of β -tetrachloro- α -ketonaphthalene as described by Weigert, the crystal axes being $a:b:c :: 0.725:1:0.504$ (128). The phototropic color change is most pronounced along the axis which lies parallel to the edges of the prism faces, i.e.,

in the direction indicated by the double pointed line, "c". Light shining from any direction may excite the phototropic change, but since the reversing light is absorbed primarily when shining in the "c" direction, polychromatic light is most effective in exciting the phototropic color change when it shines in the a-b plane, and not along the c axis. Weigert carried out this investigation with plane polarized light. The original should be consulted for details (128). These relationships have so far been developed only for β -tetrachloro- α -ketonaphthalene.

The reversing light. As has just been mentioned, light absorbed by the light induced absorption band of β -tetrachloro- α -ketonaphthalene has the tendency to reverse the action of the exciting light, that is, to cause the absorption band to disappear. This antagonistic action of light of different wave lengths acting upon phototropic substances was discovered by Stobbe in working with the fulgides (111, 112), and it has since been observed that the phenomenon is of wide occurrence among phototropic compounds, and is also observed with other photosensitive systems (104).

With all of the phototropic substances which have been examined in regard to the antagonistic effect of different radiations it has been found that the reversing light is the same or of longer wave length than the light which originally excited the phototropic change. The two effects ordinarily overlap, and light of a given wave length can serve both to excite the phototropic change and to repress it. However, in general it seems that the maximum reversing effect is shown by light of longer wave length than the light which exerts the maximum exciting effect (11, 112, 114, 115). Only a study of individual crystals such as carried out by Weigert could be expected to give accurate data on this question.

The speed with which the fading of the phototropically induced absorption band proceeds under the influence of the reversing light varies greatly with different substances.

In some cases the reversing action is very vigorous. Salicylidene aniline, for instance, hardly shows any color change in sunlight, yet if the sunlight is passed through a blue filter before shin-

ing upon the anil a strong color change, from light yellow to reddish brown, is observed. Here the substance is so sensitive to the reversing action of the long wave length rays that white light will actually cause a sample that has been darkened under a blue filter to fade.

Light is reported to have a reversing action upon the following classes of phototropic substances: The fulgides (11, 113), the stilbene derivatives (114), the anils (79, 80, 115), the complex mercury sulfides (121), and, β -tetrachloro- α -ketonaphthalene, as mentioned above. Whether or not the hydrazones and osazones show the effect is in question (11, 115).

Some quantitative studies of the reversing action of light upon some of these substances, have been made (79, 80, 115, 128).

Temperature effects. Variation in the temperature influences the phototropic process in two distinct ways: (1) it causes a change in the light absorption which induces the phototropic change; and (2) it influences the rates at which the light induced coloration and the reverse change proceed.

The wave length of the light which is effective in bringing about the phototropic change is not a constant that depends only on the nature of the phototropic substance, but depends both on the nature of the substance and the temperature of the substance. The variation in color of a substance with the temperature, or "thermotropy" as Senier has termed it, (102), is a phenomenon of wide occurrence, and is by no means limited to phototropic substances. However, certain of the phototropic substances, not only organic but inorganic (59), and other members of the same chemical groups, exhibit thermotropy to a marked degree (95, 96, 97, 98, 99, 100, 101, 102, 103, 111). The sense of the change, at least as far as phototropic solids are concerned, is such that an increase in temperature causes absorption bands to shift so as to take up light of longer wave lengths, and decrease in temperature causes the absorption bands to shift in the opposite direction. Therefore at temperatures of -100 to -200° it frequently happens that phototropic substances can be excited only by light of much shorter wave length than is required at ordinary temperatures. For instance, α -anisyl- δ,δ' -diphenyl-

fulgide when its temperature is above 22 degrees is completely excited by light of wave length longer than 2970 Å., while below -35° it is, under the same conditions of illumination, not excited by light of wave length longer than this figure (111). Stobbe has collected similar information relative to a number of other fulgides, hydrazones, and stilbene derivatives. He makes the general statement that all phototropic substances are thermotropic (115).

Padoa and his collaborators have devoted much attention to the influence of temperature on the rates with which phototropic substances change their color. Their methods of working have been to prepare for each phototropic substance, two different color standards which corresponded to the colors exhibited by the substance in different stages of excitation. The time required for the color of a substance to change from that of one of these standards to that of the other standard was determined for different temperatures. From these values, temperature coefficients were deduced. The figure given as the temperature coefficient represents the time required for the definite color change just described divided by the time required for the same color change after the temperature of the substance had been raised 10° . In determining the temperature coefficients for the light reaction, a constant light intensity was used at the different temperatures.

For determining the temperature coefficient of the light reaction it will be seen that there is a theoretical objection to this method as here outlined. While the phototropic substance is being excited by light, the dark reaction is going on, and the effect of this is to retard the light reaction. Moreover, a decrease in temperature slows up the dark reaction much more than it does the light reaction, and therefore the retarding influence of the dark reaction is relatively decreased. The temperature coefficient of the light reaction would therefore tend to appear smaller than it actually is. Practically, this objection is of little importance in view of the fact that the absolute speed of the light reaction is usually very much greater even at ordinary temperatures than the speed of the dark reaction.

As just mentioned, the influence of temperature upon the dark reaction is much greater than upon the light reaction. This seems to be very generally true of phototropic solids.

The temperature coefficients obtained by this method are listed in table 6.

Except for triphenyl fulgide the data given in table 6 for the temperature coefficients of the reactions which take place in the light all refer to the use of white light. If colored lights are used the temperature coefficient is found to vary with the color of the light (79, 80), as was predicted by Trautz (119). For salicylidene- β -naphthylamine the temperature coefficient for green light is 1.80, for blue light is 1.45, and for violet light, 1.39 (79). For benzaldehyde phenylhydrazone the temperature coefficient

TABLE 6
Temperature coefficients of phototropic reactions

SUBSTANCE	REACTION IN DARK	REACTION IN LIGHT	REFERENCE
Benzaldehyde phenylhydrazone.....	1.7	1.07	(67, 73, 78)
Piperil-o-tolylosazone.....	2.0	1.06	(78)
Benzil-o-tolylosazone.....		1.05	(80)
Salicylidene- β -naphthylamine.....	2.0	1.47	(67)
Triphenylfulgide.....	(blue light)	1.29	(80)
Diacetyl-diaminostilbene-disulfonic acid	1.65	1.07	(79)

for blue light is 1.08, and for violet light is 1.04 (80). Triphenylfulgide has a temperature coefficient of 1.67 when excited by green light (80).

The decolorizing reaction produced by the reversing light is also influenced by temperature. In the decolorization of triphenylfulgide by yellow light (6140-5740 A.) the temperature coefficient is 0.89, and for red light is 1.08 (80). There should be some wave length in between at which the reaction would be independent of the temperature. This remarkable case of a temperature coefficient of less than one has a parallel in a system described by Skrabal (108).

Another way of dealing with the effect of temperature is to consider the increase in intensity of light required to hold a pho-

totropic substance to a given color when the temperature is raised. This study has been made in some cases (67, 111). The light intensity required increases rapidly with the temperature. For instance, salicylidene- β -naphthylamine requires an increase in light intensity of 1.4 for each increase of 10° in temperature. Salicylidene-aniline requires the light intensity to be increased 1.7 for each 10° (67). These results agree with calculations based on the temperature coefficients.

Since the speed of the dark reaction increases with the temperature much more rapidly than the speed of the light reaction it will be seen that as the temperature rises a point must be reached at which the dark reaction becomes so rapid that phototropy can no longer occur, or, in other words, we reach a point at which the energy required to maintain even the slightest color change in a phototropic substance becomes enormously great. Just how accurately this "higher temperature limit," as Senier named it (103), can be determined is not known, but Senier has arrived at it within a few degrees for the phototropic anils which he has studied. One would expect the critical temperature to be a region rather than a point, something like the threshold value of a photographic plate as determined for speed measurements.

In order to show the range of these critical excitation temperatures the values which have been determined for the phototropic anils are listed in table 7. Similar data on certain fulgides, hydrazones, osazones, and stilbene derivatives are given by Stobbe (111, 114, 115), and there are other values scattered through the literature. Since these critical temperatures have not been correlated with the other properties of phototropic substances, their significance is somewhat doubtful.

It will be observed that two of the anils are phototropic only at temperatures below room temperature. One remains phototropic at temperatures above 100° .

In contrast to the behavior of these organic substances the rate of darkening of zinc sulfide does not seem to be greatly affected by temperature (11).

Photoelectric effect. Amaduzzi and Padoa (1) and Gallagher (25) have studied the photoelectric effect with phototropic sub-

stances. The original papers must be consulted for details since the results are not altogether concordant and do not permit of being condensed into generalizations.

Amaduzzi and Padoa concluded that in general, though not always, phototropic substances have more photoelectric power than substances of similar constitution which are not phototropic. From Gallagher's curves, it would seem that photoelectric fatigue is less pronounced with phototropic substances, i.e., phototropic compounds when exposed to light continue to emit steady streams of electrons longer than do similar compounds which are not phototropic.

TABLE 7
Temperature limits of phototropy in anils (103)

	HIGHER TEMPERATURE LIMIT
	°C.
Salicylidene aniline.....	50 5*
Salicylidene-m-toluidine.....	39.5*
Salicylidene-1,3,4,-xylidine.....	76*
Salicylidene-o-chloroaniline.....	82-83*
Disalicylidene-m-phenylenediamine (needles)...	75
Disalicylidene-m-phenylenediamine (plates)...	30
Salicylidene-o-bromoaniline.....	65
Salicylidene-p-bromoaniline.....	48
Salicylidene-o-anisidine.....	30
Salicylidene-p-aminobenzoic acid.....	20 (about)
Salicylidene-p-anisidine.....	Between 20 and -20
2-hydroxy-3-methoxybenzylidene-1,2,5-xylidine.	Between 0 and -20
Salicylidene-β-naphthylamine.....	Between 110 and 126

* Melting point.

Kowalski found that strontium platinocyanide which had been changed by x-rays into the phototropically excited form showed the photoelectric effect much more strongly than strontium platinocyanide which had not been exposed to x-rays (38).

If a plate covered with lithopone which has been darkened by exposure to light is connected to an electroscope and exposed to light of different wave lengths, the rate of leak of the electroscope is found to agree within a few per cent with the rate of leak when the lithopone plate is replaced by a plate of metallic zinc (11).

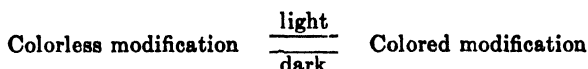
Mixed crystals. Padoa found that mixed crystals could be formed of benzaldehyde phenylhydrazone and a small proportion of benzylidene-benzylamine, and of benzaldehyde phenylhydrazone and a small proportion of diazoaminobenzene. Benzaldehyde phenylhydrazone crystals containing only very small amounts of benzylidene-benzylamine are still very phototropic. But when the anil content is increased to 5 per cent, the phototropy completely vanishes. When the content of the anil is sufficient to affect the phototropic properties, but not to extinguish the light change, the effect of the adulterant is to make the color change less pronounced and to cause the dark change to take place more rapidly than with pure benzaldehyde phenylhydrazone (63).

Amorphous mixtures. Dr. Scheiber working with Stobbe (114) prepared a number of mixtures of phototropic substances with various resins. Representative stilbene derivatives, osazones, hydrazones, anils, and fulgides were investigated. In some cases, the resinous mixtures were phototropic, in others no phototropic properties were shown. Frequently a mixture of a given resin and a given phototropic substance would be phototropic or not, depending on whether the mixture was prepared by warming the constituents together, or by precipitating them from solution. In some cases, such as that of benzaldehyde phenylhydrazone in metastyrol an inversion of the phototropic color change occurred, and the effect of light was to cause the color of the dark stable modification to fade. β -tetrachloro- α -ketonaphthalene was mixed with a number of colloidal materials. Some of the mixtures were phototropic and some were not. In some of the mixtures in which phototropy was observed there was clearly some crystallization of the phototropic substance. Stobbe believes that the behavior of β -tetrachloro- α -ketonaphthalene is such as to differentiate it from the other substances examined. In view of the inconsistencies in the behavior of the other phototropic materials when mixed with colloids this conclusion does not seem altogether beyond question.

Stobbe has also been able to stain wool, cotton and silk with fulgides and anils (113, 114). These stained fabrics are photo-

tropic, though their reaction to light is less strong than that of the original substances.

Energy relationships. While no exhaustive investigations of the point appear to have been made it is generally agreed that phototropy is a completely reversible phenomenon. The dark reaction proceeds spontaneously, and therefore, if the phenomenon is truly reversible, it must be considered that the colored modification in the typical equation,



is the colorless modification which has absorbed a certain amount of energy. Moreover, this energy must be liberated again in the dark reaction.

TABLE 8
Heats of combustion of phototropic modifications

SUBSTANCE	HEAT OF COMBUSTION		DIFFERENCE	REFERENCE
	Unexcited	Excited		
	cal./gram	cal./gram	cal./gram	
Triphenyl-fulgide.....	7810.4	7816.9	6.5	(114)
Salicylidene- β -naphthylamine.....	8291.5	8294.4	2.9	(68)
Benzaldehyde-phenylhydrazone.....	8668.8	8669.1	0.3	(68)

This line of reasoning leads directly to two questions: (1) How much more energy is possessed by the colored modification than the colorless modification? (2) In what form is the energy liberated during the dark reaction? Attempts have been made to answer both questions.

In order to determine the energy differences between the dark stable and light excited modifications of phototropic substances the heats of combustion of three substances in the two different states were measured. The results are given in table 8.

The differences are all in the expected direction, but they are so small, none being as much as 0.1 of 1 per cent of the total heat of combustion that it is doubtful if they are larger than the experimental error of the determinations. The safest conclusion

to draw is merely that the energy difference between the excited and unexcited states is very small.

From the standpoint of a reversible reaction a purely formal consideration of phototropy might lead one to expect that the energy liberated in the dark reaction would be given off in the form of light, i.e., the substances would be phosphorescent. Gallagher believed that he had observed the liberation of some form of radiant energy in the cases of disalicylidene-m-phenylenediamine and benzaldehyde phenylhydrazone (25). He described in particular the work with benzaldehyde phenylhydrazone. His evidence, which was both visual and photographic, will be discussed.

Gallagher reported three experiments made upon the action of the excited form of benzaldehyde phenylhydrazone upon photographic plates. In the first experiment the phototropic sample was placed upon a photographic plate, the whole heated to 50° for 20 minutes and the plate developed. Those portions of the plate around where the substance had been placed were found to be blackened. The second experiment was carried out like the first except that a piece of metal foil was placed below the substance. "*Cette fois, il-y-avait une image en noir de la feuille de clinquant sur la plaque et, comme dans la première expérience, les autres parties de la plaque qui, n'étaient pas en contact avec la substance étaient noircies.*" In the third experiment the photographic plate was wrapped in black paper. A piece of lead and the phototropic material were placed on top of the paper. In this case the whole plate was blackened, but in the center there appeared an image, blacker than the rest of the plate, of the piece of lead.

Working along the same lines Venkataramaiah and Janakiram made experiments with HgI_2 , 2HgS , IHgCNS , and the compound described as HSHgCNS .

The substances were taken in small capsules or phials open at one end. The mouths of these were closed with microscopic slides, numbering 1, 2, 4, 6, and 8, using sealing wax to keep them in contact with the capsules. After the compounds were excited in strong sunlight, the capsules were placed over a photographic plate and left in the dark for about two days when the compounds completely recovered. It was

observed that, as the number of slides was increased, the image produced on the plate became more and more faint and when the number exceeded twenty, the image became imperceptible. . . . It is curious to note that in every case it was the positive that was printed on the plate (124).

Presumably the last sentence means that where the plate was actually protected by contact with a cover glass there was no blackening; the blackening took place around the edges of the cover glass.

Such photographic evidence of radiant energy as that obtained by Gallagher and Venkataramaiah and Janakiram is anything but convincing, and has the earmarks of the Russell Effect. Gallagher did not describe his photographic results very clearly, and his plates were not reproduced with his article. However, his results certainly do not preclude chemical fogging of the plates. Benzaldehyde is known to produce the Russell Effect (37), and the benzaldehyde phenylhydrazone itself is readily oxidized by air (116). In his third experiment the black paper very possibly caused fogging. Venkataramaiah and Janakiram's account of their experiments is as clear a description of the Russell Effect, caused by the sealing wax (87, 120), as could be desired.

Stobbe found that during the dark reactions the fulgides (111) produced no image upon a photographic plate. The stilbene derivatives chemically fog a plate but give no evidence of emitting light (115). Cinnamicaldehyde semicarbazone is without action on a photographic plate.

Gallagher's further observation was that if light excited benzaldehyde phenylhydrazone were placed on a watch glass and both heated to 100° the watch glass glowed (25).

Zanella (132) was unable to obtain the fluorescence of the watch glass which Gallagher reported. He also found that the dark stable form of benzaldehyde phenylhydrazone behaved exactly the same toward a photographic plate as the light excited form. The plate was fogged, just as Gallagher found, if only the black paper was interposed between the plate and the phototropic substance. However, if there were interposed between

the photographic emulsion and the phototropic substance a perforated brass plate 0.7 mm. thick, a gypsum plate a few tenths of a mm. thick, and a glass plate a few thousandths of a mm. thick, there was no action upon the photographic plate. Zanella concluded that the action observed by Gallagher upon the photographic plate was due purely to some chemical decomposition of the phototropic substance.

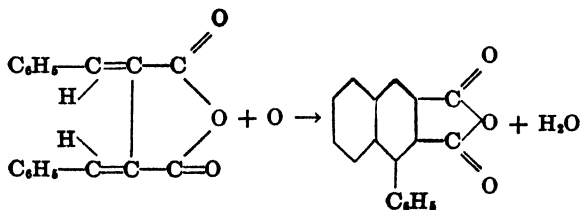
The luminescence of the watch glass observed by Gallagher is difficult to understand. It is not impossible that his watch glass was thermoluminescent.

The energy relationships are of importance to an understanding of the mechanism of phototropy, and it is unfortunate that so little concordant data are available.

Chemical relationships. The relations between the constitution of substances and the occurrence of phototropy has already been dealt with in listing the known phototropic compounds. In addition to these observations, certain other parallelisms between phototropic and purely chemical phenomena have been noticed. Many phototropic substances appear to be relatively little affected chemically by long exposure to light. Thus benzaldehyde phenylhydrazone shows only a few degrees lowering in melting point after exposure to daylight for a whole summer, and after exposure it can readily be identified as still benzaldehyde phenylhydrazone (14).

While benzaldehyde phenylhydrazone shows no change in melting point on passing from the colorless to the excited red modification, the melting point of benzaldehyde-o-tolylhydrazone changes from its original value of 100° to 102° to 80° to 83° for the excited form. Benzaldehyde-p-tolylhydrazone also shows a change of melting point of from 114° to 101° (86).

Diphenyl fulgide, is completely decomposed by long exposure to light, and Stobbe reports that it reacts as follows (110, 113):



The sodium salt of diacetyl-4,4'-diamino-stilbene-2,2'-disulfonic acid appears to exhibit phototropy only in an atmosphere containing oxygen, and when this substance is exposed to light in an oxygen containing atmosphere, some of the oxygen is converted into ozone (115). The light which effects this reaction is of longer wave length than that required to convert oxygen directly into ozone. It is an interesting case of photo-sensitization. This observation also throws some light on the energy relationships since ozone is an energized form of oxygen.

Hexanitrodiphenylamine also requires an oxygen containing atmosphere in order to exhibit its phototropy (114), but in this case, it is not known whether or not the oxygen suffers any change.

Cinnamicaldehyde semicarbazone too requires oxygen (33).

β -tetrachloro- α -ketonaphthalene, and the osazones which have been investigated are phototropic whether they are placed in a vacuum or in an atmosphere of air, or oxygen, or hydrogen, or carbon dioxide (114). With the osazones the presence of oxygen in the surrounding atmosphere seems to have a slight inhibitory action on the color change produced by light.

Various hydrazones, anils, and fulgides are reported to be phototropic in air, oxygen, hydrogen and carbon dioxide, but not in a vacuum (114). The latter is a very curious observation, and is a distinction from the behavior of the osazones and the chloronaphthalene.

The presence or absence of moisture in the surrounding atmosphere seems to have very little effect upon the phototropic properties of any of the substances investigated, i.e., stilbene derivatives, the tetrachloro ketonaphthalene, hydrazones, osazones, anils, fulgides, and hexanitrodiphenylamine (114, 115).

Lithopone will darken when exposed to light only if it is moist. When it has been darkened by the action of light, it requires the presence of oxygen in order to undergo the reverse change in the dark. That is, the substance can be darkened by light in the absence of oxygen, but oxygen or an oxidizing agent is required for the fading which takes place in the dark (12, 41, 60, 83). Lead acetate, ammonia, formaldehyde, and other reducing agents increase the light sensitiveness (11, 41, 60).

When a gelatin film stained with methylene blue is bleached by exposure to light the presence of oxygen is necessary in order that the change may be reversible. In absence of oxygen, the bleaching is more rapid, but the color does not return in the dark (39).

Fatigue. On prolonged exposure to light phototropic solids show more or less pronounced fatigue, that is prolonged exposure causes them to undergo the phototropic change less readily or not at all.

The readiness with which phototropic substances fatigue varies greatly with the substances. Benzaldehyde phenylhydrazone (12) and some, at least, of the fulgides (111, 113, 114) fatigue very quickly. $\text{HgI}_2 \cdot 2\text{HgS}$ (121) and lithopone (82) also show fatigue. In all of these cases the fatigued modification is as light in color, or lighter, than the original dark-stable form. The light first produces the excited colored form of the compound, and then, if the action of light is continued long enough, the color fades until it may be even less pronounced than the color of the original unexcited material. On the other hand, various anils fatigue to darker modifications (96, 97).

Contrasted with these cases of more or less readily produced fatigue, some phototropic substances appear to suffer very little fatigue on exposure to light. Salicylidene aniline, in a sealed Pyrex tube, shows no change in phototropic properties on exposure to daylight for a year.

Profound chemical change may accompany the appearance of fatigue, as in the cases of di- and triphenyl fulgide, mentioned above. On the other hand, a substance may fatigue readily and yet not suffer great chemical change. The latter phenomenon is shown by, for instance, benzaldehyde phenylhydrazone. If a sample of this substance is exposed to light for some time, the red color originally produced by light gradually fades, and the substance, although still exposed to bright light, becomes colorless. However, the melting point does not change greatly, and if the crystals are broken in a mortar, the sample regains its phototropic properties (14).

PART II. THEORETICAL

General. From the resumé of experimental results which has been given, it will be seen that a number of very diverse substances show the phototropic change. In certain cases, definite mechanisms have been developed to account for the color changes exhibited. With the phototropic liquids, whose behaviour has been explained at all, a chemical mechanism is involved. With some of the solid substances, such as lithium imide, and lithopone, we have what appear to be more or less adequate chemical pictures which will account for the phenomena observed. In another case, that of the stilbene derivatives, we have evidence of a chemical change accompanying a phototropic change.

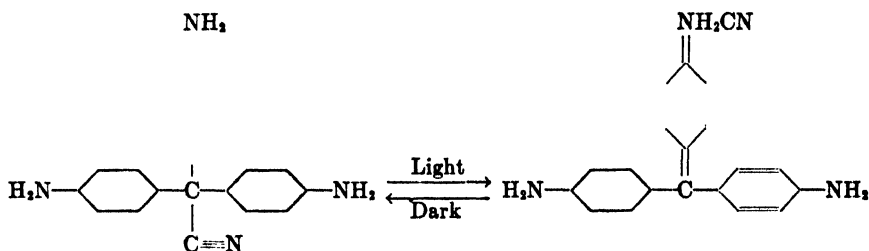
There still remain the classes of phototropic substances which have been most extensively investigated, namely, the fulgides, the anils, the hydrozones, the osazones and β -tetrachloro- α -ketonaphthalene. These substances seem to be more or less closely associated as regards their phototropic properties, and it is on these substances that most thought has been expended in order to develop adequate theories of their behaviour. There is still a lack of agreement among the scientists who have investigated the phenomena of phototropy as to the explanation of the behaviour of these compounds.

In the following summary of theoretical considerations, the various types of reactions which have been proposed for the different instances of phototropy will be discussed independently. Except for the last large class of substances, there is no great disagreement as to the explanation of the behaviour of the compounds. There is often a paucity of material to go on and a certain amount of unfounded conjecture.

Dye derivatives. The triphenylmethane dyestuff cyanides, carbinols, and sulfites are assumed by Hantsch to have two forms, but have the one colored and ionizable, and the other colorless and unionized. Hantsch established a parallelism between the loss of color and the loss of ionizing ability when these dye derivatives were first formed and changed into the colorless modifications (31). These ideas have been extended by others, especially as regards the relation of ionization to color (50).

Following this idea of dual forms of the dye derivatives, Lifschitz believes that the colorless form is stable in the dark in solution but that the action of light converts it into the colored form (42). He has followed through, as already described, the relation between the development of color in the light and the development of electrical conductivity in the solutions of these dyestuff derivatives.

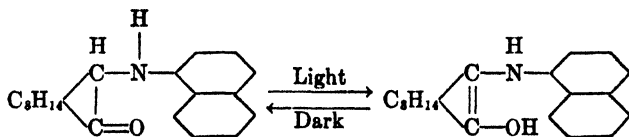
We, therefore, have as the mechanism of the phototropic change, the following reactions:



Although this chemical mechanism appears to be adequate, it does not give us a complete picture of the reaction since the energy relationships are left unexplained. The colored, ionized form may be inferred from the work of both Hantsch and Lifschitz to have a higher energy content than the unionized, colorless form. What becomes of this energy when the colored form changes into the colorless is not known.

Camphor derivatives. With these substances, Singh has established a parallelism between the color of the solutions and the optical rotation.

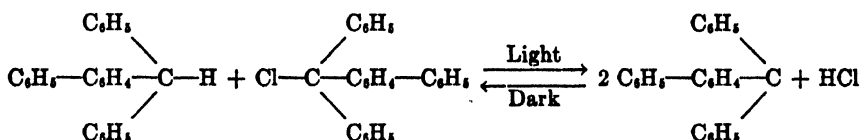
Singh believes that we have the following chemical equilibrium which, as indicated, is displaced by light so as to produce the enol form (105, 106):



He also finds that the light produced modification has different chemical reactions from the normal stable form, and relies on his

reactions with ferric chloride to substantiate the keto-enol tautomerism of these substances. He believes that the green color of the solutions which have been exposed to light results from a mixture of the keto and enol forms, which may be independently colorless, but which he believes form a colored combination similar to quinhydrone (106).

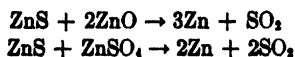
Triphenyl methane derivatives. The solutions of triphenyl methane derivatives, which change their color in light, are supposed to undergo the following reactions (91):



To substantiate this view, it is pointed out that diphenyl-monobiphenyl-methyl and phenyl-dibiphenyl-methyl in benzene solution are relatively sensitive to hydrogen chloride, but are stable to sun-light (91).

Ferrocyanide solutions. The coloration produced by light in a solution of potassium ferrocyanide and phenolphthalein is said to be due to the formation of alkali, potassium hydroxide, by light. In the dark the potassium hydroxide is reneutralized and the phenolphthalein loses its red color (4).

Lithopone. Phipson originally suggested that lithopone might contain a compound of an unknown photosensitive element for which he proposed the name actinium, but nothing ever came of this suggestion. Cawley suggested that the blackening due to the action of light on lithopone is caused by the formation of metallic zinc in the lithopone (12). He proposed the reactions:

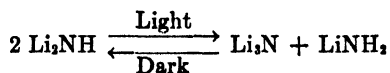


Evidence for Cawley's view that zinc is formed is the fact discovered by Phipson that oxygen was required for the color of lithopone to bleach again in the dark (83). This view has been further extended and generally adopted by others (11, 41, 46, 60). Brickwedde found that lithopone darkened by the pres-

ence of metallic zinc which had been distilled upon its surface, bleached just as fast in the dark as lithopone which had been darkened by exposure to light. As further evidence, he presents the parallelism between the photoelectric effect shown by lithopone darkened by light and a plate of metallic zinc. His theory is that light acts upon the zinc sulfide in lithopone to produce metallic zinc and hydrogen sulfide. As evidence to substantiate this, he points out that lithopone is more sensitive to light when it is moistened with lead acetate solution (11).

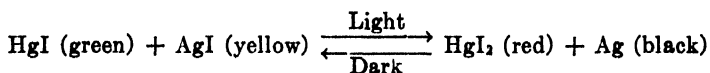
However, the actual reaction involved is still a matter of conjecture. Each investigator has had his own opinion, and this had seldom agreed with that of anyone else. Phipson believed in "actinium"; Cawley in the formation of SO_2 ; Brickwedde in the formation of H_2S ; and Lenard in the formation of zinc and sulfur. Weiser and Garrison say that Lenard's view is absurd, but wisely refrain from committing themselves to any specific chemical reaction.

Lithium imide. The mechanism proposed by Dafert and Miklauz (16) is the following:

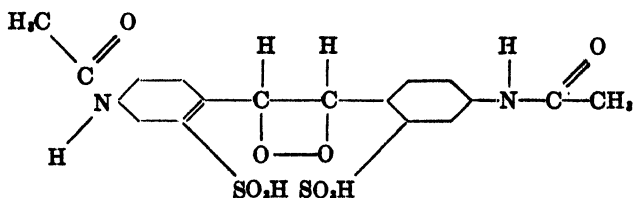


Lithium nitride is known to be brown and is known to react with lithium amide as indicated for the dark reaction.

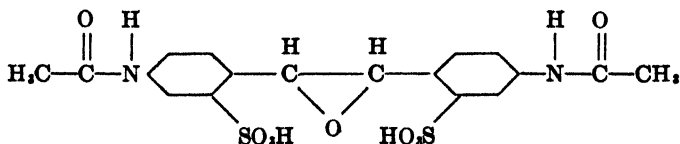
Silver and mercurous iodides. The phototropic mixture of silver iodide and mercurous iodide formed by toning a silver photographic image with mercuric iodide is supposed to undergo the following reactions (23):



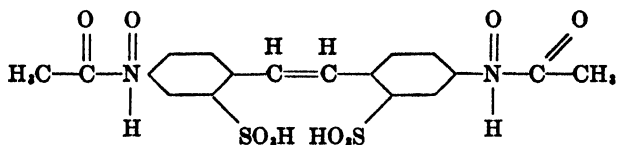
Stilbene derivatives. Stobbe assumes that when the phototropic stilbene derivatives are exposed to light they take up oxygen to form a colored organic oxide which may have the structure of an organic peroxide:



or of an ethylene oxide:



or of an amine oxide:



In the dark, the oxide, whatever form it may have, is assumed to revert to the original stilbene compound with the liberation of ozone.

As further support of this theory, Stobbe quotes the findings of Padoa (79), who concluded from the rate of color change of the stilbene derivatives that the reaction produced by light is bimolecular.

The theory has a great advantage over all the other theories that have been proposed in that it accounts for the energy as well as for the possible chemical mechanism. Its weak point lies in the fact that the colored oxides have never been isolated and identified.

Anils, hydrazones, osazones, fulgides and β -tetrachloro- α -ketonaphthalene

This most investigated group of phototropic substances has been the subject of much speculation and some critical investigation. While there appears to be no conclusive evidence that

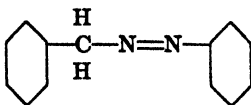
these substances in their phototropic mechanisms form a homogeneous group, most of the investigators have tacitly assumed that these compounds are to be considered together. The reasons for this grouping would appear to be: (a) that these are all pure substances and form pleochroic crystals; (b) the lack of a really satisfactory explanation for the phototropic behavior of any of these substances; and (c) that these are the best known phototropic compounds.

The hypotheses which have been advanced may be divided into those which postulate a purely physical mechanism and those which postulate a purely chemical mechanism.

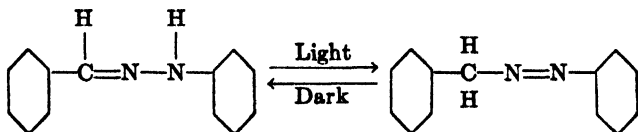
Physical theories. In his original paper on phototropy, Marek-wald (47), having observed that only one of the two crystalline modifications, and none of the solutions or melts, of β -tetrachloro- α -ketonaphthalene was phototropic, and that the phototropic change involved an increase in the pleochroism of the crystals, concluded that the phenomenon was bound up with the crystal form, and was purely physical. To give further support to this idea, Weigert (128) pointed out that only one of the two tetrachloro-ketonaphthalenes prepared by Zincke (133) was phototropic, that solutions of the phototropic substance showed the same absorption band as the crystals, but were not phototropic, and that the action of light did not cause a distortion of the phototropic crystals. He again called attention to, and considered in great detail, the pleochroism of the crystals. Stobbe has further shown that the phototropic properties of β -tetrachloro- α -ketonaphthalene remain constant regardless of the nature of the surrounding atmosphere or its pressure (114).

Weigert concluded from his own investigations that the phototrophy of β -tetrachloro- α -ketonaphthalene could be accounted for by his general theory of photochemical action (127). The theory, in its details, cannot be adequately summarized in a brief review, and the original papers (127, 128) should be consulted. Weigert's basic conception is that the absorption of light causes a distortion of the electronic orbits within the phototropic crystal, and that this distortion results in an anomalous absorption of light.

Gallagher synthesized the substance:



and found that this was stable, both in the dark and in the light (24). From this he concluded that the phototropy of benzaldehyde phenylhydrazone could not be due to the isomeric change:



This observation was advanced as further evidence that the phototropic change in benzaldehyde phenylhydrazone is purely physical and not accompanied by a chemical reaction. From his work on the photoelectric effect, Gallagher (25) concluded that the loss of electrons suffered by phototropic substances when they are exposed to light, causes a change in light absorption—just how is not altogether clear.

Chemical theories. The chemical theories all assume that the weakly colored phototropic materials which are stable in the dark are converted by light into new chemical substances which are more strongly colored. It is further assumed that in the dark these new chemical compounds change back into the original substances. The theories differ in their assumptions as to just what the new chemical substances formed by light may be. All of the chemical theories suffer from the handicap that no one has been able to isolate or identify, or even conclusively show, the existence of the hypothetical new compounds formed by light. Of course, ultimate photochemical decomposition products have been obtained, but these are not phototropic.

Chattaway (14) believed that benzaldehyde phenylhydrazone was converted by light into a colored isomer, and suggested the equilibrium:



Gallagher's work referred to above was designed to show the fallacy of this particular assumption.

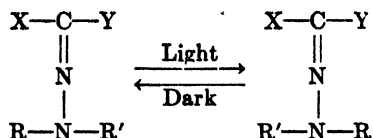
Stobbe also believes in the formation of a colored isomer of some sort in the case of the fulgides (111, 112), and he suggests that the action of light may be to convert a fulgide into a stereoisomeric form and that this form reverts to the original on standing in the dark. He showed that light did convert some fulgides into their stereoisomers: however, the reverse change in the dark does not appear to have been demonstrated, and it would seem that the isomers produced by light are not the colored phototropic forms (113).

Stobbe differentiates between β -tetrachloro- α -ketonaphthalene and the anils, fulgides, hydrazones, osazones and stilbene compounds on the basis of his experiments with amorphous mixtures of the substances, and the behavior of the substances in vacuum (114). He concedes the purely physical nature of the phototropic change in β -tetrachloro- α -ketonaphthalene, and believes that the change in the other classes of compounds is purely chemical. He has considered the formation of a new substance in a photosensitive crystal, and believes that up to a certain relatively high concentration the new substance would form a solid solution in the mother crystal without affecting the crystal structure. Padoa also believes in the possibility of forming such solid solutions, and has experimentally demonstrated the correctness of this view (65).

Senier and Shepherd considered that the phototropic change was an isomerism (101), and more specifically a case of polymerization (102, 103, 104). They assume "the existence of complex solid molecular aggregates related to gaseous molecules as gaseous molecules are related to atoms." (103) A change in aggregation is caused by exposure to light, and this change is reversible. It is further implied that the different aggregates have different colors. Senier and Shepherd believed that the chemical change involved must be very simple because of the ease with which the anils form colored modifications not only under the influence of light but also as a result of the action of heat, crystallization from different solvents, and through other agencies. By crystalliza-

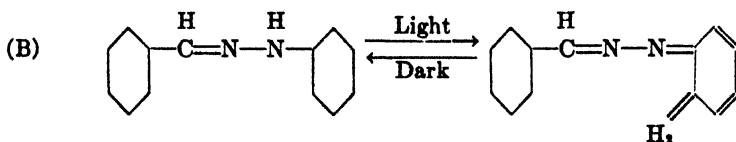
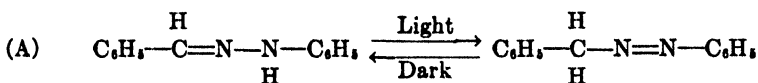
tion from concentrated solutions, they actually prepared a red modification of salicylidene- β -naphthylamine, which appeared to be identical with the phototropic form produced by light (103). They consider that their hypothesis offers an adequate mechanism, but they adduce no direct evidence to support it.

Graziani and Bovini observed that the hydrazones derived from diphenyl and ditolyl hydrazines were never phototropic even though the corresponding hydrazones derived from the monophenyl and mono tolyl hydrazines were phototropic. On the strength of this observation, they proposed a new type of isomerism in hydrazines (28):



Such an isomerism, if it occurred, might account for the necessity for different substituents in a disubstituted hydrazine in order to form phototropic hydrazones. The known syn-anti isomerism would not account for this.

It then occurred to Graziani and Bovini to check up their theory by actually preparing hydrazones from disubstituted hydrazines in which the two substituents were different. They prepared a number of hydrazones from phenyl-benzyl hydrazine, phenyl-methyl hydrazine and phenyl- β -naphthyl hydrazine. Not a one was phototropic (29). There being no longer any excuse for their first theory, Graziani and Bovini suggested two alternative mechanisms (29):

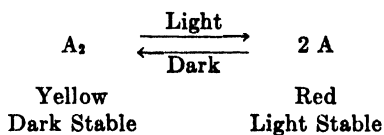


The authors preferred scheme "B," because they believed that this agreed best with the observation that no hydrazone derived from an aldehyde monosubstituted in an ortho position was phototropic. Just why the second ortho position could not react according to scheme B is not clear.

The first mechanism had already been proposed by Chattaway, and was discussed above. The second mechanism is safe from attack for the present since no one knows how to prepare the hypothetical product.

As a result of his studies upon the velocity of color change in both the light reaction and dark reaction of various phototropic substances, Padoa concluded that light produced a monomolecular reaction in salicylidene- β -naphthylamine and benzaldehyde phenylhydrazone, and that the decolorizing reaction which took place in the dark with these substances was bimolecular.

From this evidence, Padoa believes that the phototropic change involves a polymerization and depolymerization, and that the weakly colored dark stable forms of salicylidene- β -naphthylamine and benzaldehyde phenylhydrazone are the dimers of the more strongly colored light stable forms (73):



Discussion. While this paper is essentially a review, it may not be out of place to point out certain factors which have been implied in the work reviewed although they have not been specifically discussed by the various investigators.

In the present state of knowledge the distinction between a purely physical mechanism for phototropy and a purely chemical mechanism is not very clear, and is certainly unprofitable. It is a question if the mechanism proposed by Weigert could operate without involving what might be considered a change in chemical relationships, and on the other hand, a "purely chemical" photo-reaction is inconceivable.

The divergent views of the investigators has led to a certain

lack of coördination in the researches. The physical aspects of the phototropy of β -tetrachloro- α -ketonaphthalene have been most carefully investigated by Weigert, yet this substance has not been subjected to such investigations as those relating to the velocity of the color change which have been made to acquire some knowledge of the chemical relationships involved. On the other hand the anils, hydrazones and fulgides have not been given as careful a physical examination. Therefore, while a good deal of information is available on a variety of different substances, there is not the same breadth of information on any one substance or class of substances. As there is always the possibility that the mechanism is different in different cases, it is difficult to utilize the data available for the formulation of a complete theory, and the theories which have been proposed, or which could be proposed on the basis of the present knowledge, all suffer from this state of affairs.

It is generally agreed that the phototropy of these substances is bound up with the solid, if not definitely crystalline, state. In fact, these substances may be considered to form what might be called the pleochroic group. The name does not imply that other phototropic substances will not be found to be pleochroic, but that among the substances of this group the phototropism is known to be exhibited in an increased pleochroism of the crystals.

The very fact that the phototropic change manifests itself in an increased pleochroism of the crystals might at first sight seem to exclude the possibility of the change being due to the formation of a new colored compound, for it would be expected that light absorption due to molecular structure would be the same in all directions, whether or not the colored compound might be in solid solution in another substance. However, the situation is not so simple as it may at first appear. The distribution of the color throughout the phototropically excited crystal is not uniform, but the crystal becomes colored only where the light has acted. As was carefully pointed out by Wiegert, the phototropically excited crystal always shows some color change no matter in which direction it may be looked through. The change is much greater in one direction than in the others, but there is some changes along all of the axes.

Before it can be concluded that the substance of the crystal is always actually anisotropic as regards its light absorption it must be shown that the pleochroism of the excited crystals is not due to the distribution of the color in the crystal. This has not been done except with the chloronaphthalene compound. It is quite conceivable that when the excited crystal is looked at lengthwise, in which direction it shows the greatest color change, the light which passes through the crystal travels through the colored layers parallel to their surfaces, and, therefore, suffers the maximum absorption. When the crystal is looked at from the side, the light may pass through the colored layers perpendicular to their surfaces, and, therefore, through the least possible amount of colored material.

Even if it were shown that no new colored compound were formed in the phototropic reaction, it would not necessarily follow that the reaction was independent of the formation of a new substance. The photochemical production of a new compound within a photosensitive crystal is known to produce mechanical strains (65), which would seem to be similar in many respects to the strains pictured by Weigert as the cause of the color change. Such a mechanism would reconcile the evidences of chemical reaction accompanying the phototropic change with a physical picture similar to that proposed by Weigert.

In point of fact, there is no direct evidence of the formation of new substances as the result of the action of light on these phototropic materials, or of the "electrochromism" postulated by Weigert or "piezochromism" suggested above. The whole problem needs further investigation by the combined methods and view points of physics and chemistry. It would seem that the alchemistic axiom, "*corpora non agunt nisi liquida*," would have to be forgotten for this work and the reactions investigated in the solid phase since they do not appear to occur in liquids; but phototropy furnishes an interesting field for investigation by the chemist who is interested in solid phase reactions. The purely physical investigation would seem to lie along more familiar lines, since if the light produced distortion of the electronic orbits within a crystal can cause color, it should be possible to

produce the distortion and color change by other agencies than light. In fact, it has already been found that the color change can be produced in salicylidene- β -naphthylamine by rapid crystallization from solution (103), though whether this can be considered an instance of distorted crystal forces is open to question.

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THE MECHANISM OF CARBOHYDRATE OXIDATION¹

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The carbohydrates are a group of chemical compounds which have always been of great theoretical interest to the student of organic chemistry. The splendid contributions from this area of our science have become milestones in general chemical progress. The literature of chemistry has been constantly enriched throughout the years by the solution of many difficult problems concerning the molecular architecture of various kinds of sugars. As a present moment example, may I remind you of the masterly contributions now being made with reference to the structure of the disaccharides. Recall, if you please, the recent startling announcement that the synthesis of sucrose had been finally achieved. An enumeration of the workers who have labored in the field of carbohydrate chemistry would constitute a brilliant array of names.

As rapidly as the structural and synthetic questions have been gradually cleared up the demand has been insistent that we place an increasing emphasis on a better understanding of the reactions of the carbohydrates more especially that of oxidation. By reason of both its theoretical and biological significance this latter chemical change needs our most earnest attention. In attempting work in this direction it was hoped that the oxidation mechanism of these complex substances could be traced more surely by using the data which we had obtained in some earlier experiments with compounds of the more simple type. The necessity for scientific work of this character seems to find a complete justification in the recent significant statement of one of your own distinguished members, Dr. P. A. Levene (1), who

¹ The William H. Nichols Medal Address for 1929, delivered before the New York Section of the American Chemical Society, March 1, 1929.

said: "Glucose is one of the most important substances in the economy of the world."

In placing before you the results of the researches upon which the Jury of Award of the William H. Nichols Medal rested its decision for 1929, may I briefly recall at least two of the important characteristics of the period in which our earlier work was undertaken nearly a quarter of a century ago. One of these was the rapid expansion which was beginning to take place in the realms of physical chemistry. A number of causes contributed to this increasing activity. In the eighties Arrhenius announced his views with reference to the nature of electrolytes. In the nineties a group of important discoveries were made which were destined to exercise a marked influence on the views then held concerning the fundamental nature of material things. As you are aware, reference is here made to the radioactive elements, the rare gases of the atmosphere, the Roentgen ray, and the electron. These were memorable events. They did much towards focusing the interest of investigators on the physical aspects of chemistry. Many of us recall the profound impressions which these far reaching discoveries made on the scientific world at that time.

The influence of this growing interest in physical chemistry immediately began to bear fruit in the field of reaction mechanism. The application of the Law of Guldberg and Waage to some of the postulates of the newly enunciated solution theory gave a satisfying starting point for a better understanding of inorganic chemical reactions. The importance of this contribution to our knowledge of reaction mechanism and the incentive which it proved to be for many workers can hardly be over-emphasized. The present efforts which are being made to successfully utilize the electronic conceptions of matter in formulating a sound theory of chemical behavior should receive the most sympathetic encouragement.

On this occasion it is of much interest to note that it was in these years that Dr. Claude S. Hudson began his work on the use of physical chemical methods in the solution of carbohydrate problems. His contributions in both that field and also in that of the more strictly organic character have won for him a place

of distinguished leadership, which has received the highest recognition of his fellow scientists.

The second of these movements which characterized the opening years of this century was the continued vigor with which the classical organic synthesis was extending its conquest in every direction as it had been doing for many years previously. It is well known that this great activity produced a constantly increasing number of compounds of the element carbon.

Many new questions began to arise from this constant multiplication of new compounds. Prominent among these were the phenomena which are now grouped under the familiar name of *tautomerism*, a concept to which we shall have occasion to refer at several important places in our discussion. Another problem which was constantly demanding more attention was the great need of a satisfying theory of organic chemical behavior. The triumphs of the ionization theory in the field of inorganic chemistry only served to accentuate this need. Three theories of chemical behavior were claiming the attention of the organic chemists at this time. One of these was the fruitful partial valence theory of Thiele. The other two were those fostered by the Americans, Arthur Michael and the late John Ulric Nef. The problem still confronts us. Out of the continued efforts of these many years and with a continued zeal in chemical research aided by modern methods of attack, it is hoped that a simple and helpful theory of organic chemical behavior may finally be evolved.

Such, in brief, was the spirit of chemical science when we undertook in the Chemical Laboratory of The Ohio State University a study of the oxidation of organic compounds. The principal objective in these experiments was the determination of the molecular stages through which organic compounds passed when they were subjected to oxidizing conditions. In pursuing this line of investigation it was desired to test Nef's (2) theory of organic chemical behavior from the standpoint of its usefulness in coördinating facts already known as well as to test its power of predicting unknown chemical behavior. It was hoped that this brilliant investigator's views might thus serve as a means of

establishing some useful generalizations concerning the oxidation of organic compounds.

To accomplish these ends it became necessary to conduct all our experimental work under very carefully chosen conditions. The accurate methods of quantitative analysis were used in gathering the experimental facts. In our latest work with the carbohydrates we have been confronted with the problem of quantitatively separating certain reaction products which were very closely related to one another. Obviously, this challenge is a difficult one in some cases yet withal it is one full of interest.

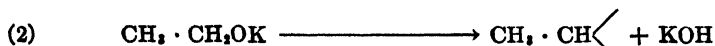
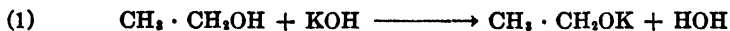
ETHYL ALCOHOL AND ACETALDEHYDE

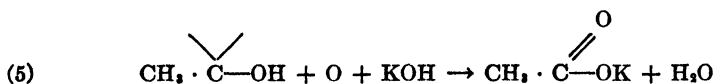
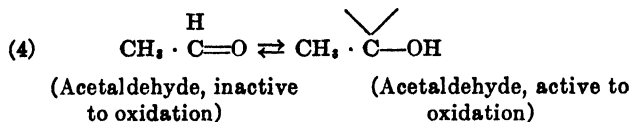
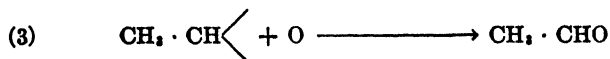
The first substance to be studied in this general manner was ethyl alcohol. This compound was oxidized with aqueous solutions of potassium permanganate in the presence and in the absence of added potassium hydroxide. An examination of the literature of this particular reaction disclosed the fact that previous investigators had found the following compounds among the oxidation products: acetaldehyde, formaldehyde, oxalic and acetic acids and carbon dioxide. The point of interest in all this work was the notable fact that the presence of added alkali seemed to be necessary for oxalic acid formation, although Chapman and Smith (3) reported the presence of this acid even in the absence of any added alkali. Morawsky and Stingl (4) believed that temperature merely influenced the rate of the reaction, while Pean de Saint Gilles (5) was of the opinion that the temperature was also an important factor in determining both the character and the amounts of the products formed. No complete systematic study had been previously made of the permanganate reaction for the purpose of ascertaining the effect of temperature and the alkali concentration on the character and the amounts of the oxidation products. We found that carbon dioxide, acetic and oxalic acids were the only reaction products when the alcohol was oxidized under the experimental conditions which we adopted (6). Acetic acid was the sole product in the absence of any added alkali. Our data accounted for a quantitative return of the carbon introduced as alcohol. A consideration of our quanti-

tative results showed that the yields of these oxidation products were functions of the initial concentration of the alkali used and of the temperature employed.

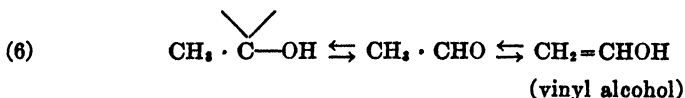
In order to gain an insight into the exact reaction mechanism which produced these results, it was found necessary to subject the various oxidation products of ethyl alcohol which were theoretically possible to exactly the same experimental conditions as those used in these oxidations. As is well known chemical theory indicates that the formation of acetaldehyde is the *first step* in this oxidation mechanism, while the formation of acetic acid is regarded as the *second step*. An accurate experimental study of acetaldehyde (7) showed that this first intermediate behaved in the same general manner as did ethyl alcohol, i.e., the amounts of the reaction products were found to be functions of the same experimental conditions as those surrounding the oxidation of the alcohol. Hence it may be safely concluded that acetaldehyde is the first oxidation product of ethyl alcohol in neutral and alkaline potassium permanganate, and that the acetic acid is derived from the acetaldehyde.

From the general character of our quantitative data it is clear that the alkali must play an important rôle in the oxidation mechanism of ethyl alcohol. As the concentration of the potassium hydroxide is increased the alcohol molecules seem to become much more sensitive to attack. According to Nef's views (8) the alcohol and the alkali react to form an alcoholate which in turn is dissociated into ethylidene with much greater ease than is the ethyl alcohol itself. Hence, the mass action effect of the alkali would increase the speed of the ethylidene formation. The unsaturated compound thus formed would be oxidized to acetaldehyde. The acetaldehyde thus formed is undoubtedly in equilibrium with its enolic form which may be regarded as the *active form* of this molecule (9). This enol is easily oxidized to acetic acid. It is clear that the tendency of the alkali would be to increase the velocity of this change. These changes are shown in the following equations.





Our next logical step was to find the sources of the other two products, oxalic acid and carbon dioxide. A consideration of quantitative data obtained from a study of the oxidation of potassium acetate (10) showed conclusively that this salt could not be seriously regarded as a source of these two oxidation products. Since acetaldehyde had been oxidized with potassium permanganate in the absence of alkalis to acetic acid exclusively it was thought best to make an accurate quantitative study of the conditions which give rise to vinyl alcohol formation when acetaldehyde is treated with aqueous solutions of potassium hydroxide, i.e., study the behavior of acetaldehyde towards potassium hydroxide itself in the absence of potassium permanganate. A knowledge of these data became the more desirable since it had long been known that vinyl alcohol possessed a structure which was most easily attacked with alkaline potassium permanganate. Much to our satisfaction we found that vinyl alcohol production from acetaldehyde in the presence of an aqueous solution of potassium hydroxide was a linear function of the alkali concentration (11). Therefore, it must be concluded that in the oxidation of ethyl alcohol there is an equilibrium existing between acetaldehyde (active form), acetaldehyde (inactive to oxidation), and vinyl alcohol which may be shifted in the direction of vinyl alcohol by an increased concentration of alkali. It is



clear that such a change would result in diminished yields of acetic acid and increased yields of oxalic acid and carbon dioxide,

a point of view which is in harmony with our results. It is interesting to point out that a definite concentration of alkali was found to be necessary before oxalic acid formation began. On the basis of the relationship existing between the concentration of the potassium hydroxide used and the amounts of acetic acid formed we were able to calculate these values (12). By experimentation we found that the limiting upper value for the alkali concentration which would still yield the maximum amount of acetic acid was between 0.415–0.461 gram per liter. Our calculation gave 0.46 gram. Hence, it was concluded that vinyl alcohol must be the next intermediate after acetaldehyde in the series of reactions producing oxalic acid and carbon dioxide when ethyl alcohol is oxidized with potassium permanganate in the presence of alkalies. Since vinyl alcohol has a momentary existence only, it also became necessary to study its theoretically possible oxidation products for the purpose of establishing that this alcohol is an intermediate in these reactions producing oxalic acid and carbon dioxide. These were glycolic aldehyde, glyoxal, glycolic acid and glyoxylic acid. All of these yielded oxalic acid and carbon dioxide in amounts which showed that complete oxidation had taken place. Furthermore, it was found that the yields of these products were related to the alkali concentration in the same general manner as had been observed with ethyl alcohol and acetaldehyde (7). The neutralization of the acids formed in these changes is obviously an important factor which will influence any equilibrium conditions that may arise in such systems as those studied.

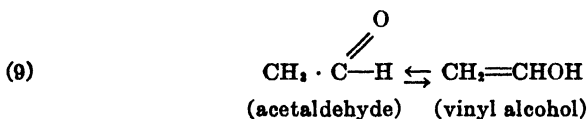
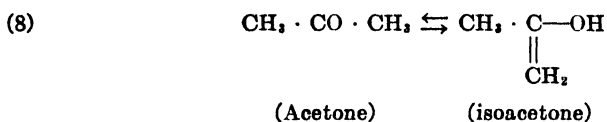
ISOPROPYL ALCOHOL AND ACETONE

We next investigated the behavior of isopropyl alcohol (13) and acetone (14). Precisely the same procedures and general experimental conditions were used as had been employed with ethyl alcohol and acetaldehyde. Carbon dioxide, acetic and oxalic acids were found to be the oxidation products both in the presence and in the absence of added alkali. A small amount of acetone was also found at 25°. As had been the case with ethyl alcohol and acetaldehyde, temperature and alkali concentration were the important factors controlling the character and

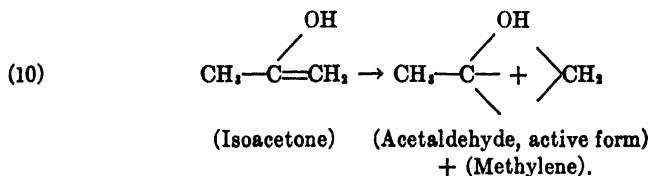
the amounts of oxidation products formed from isopropyl alcohol and acetone. One notable difference was found in the products obtained from these two pairs of compounds. With neutral potassium permanganate, oxalic acid was always found as an oxidation product of isopropyl alcohol and acetone, while as shown above, this acid was absent in the oxidation products of ethyl alcohol and acetaldehyde with the same reagent.

A study of the intermediates which might conceivably be formed in the oxidation of isopropyl alcohol showed that acetone must be the first oxidation product formed in this reaction. This arises from the fact that none of the possible intermediates save acetone will yield all the products which isopropyl alcohol will give. Therefore, it is clear that the source of the oxidation products must be sought for in those chemical changes through which acetone passes when it is oxidized under the same conditions. The reaction mechanism of acetone formation from isopropyl alcohol is analogous in every way to the formation of acetaldehyde described above; namely, isopropylidene is the unsaturated intermediate.

These results are best understood on the ground that the added alkali reacts on acetone in the same general way as it does on acetaldehyde, i.e., it shifts the equilibrium existing between acetone and isoacetone molecules in the direction of the isocompound. In order to test this point of view we studied its behavior in the same general manner as we did that of acetaldehyde; i.e., its action towards aqueous solutions of potassium hydroxide in the absence of potassium permanganate. Again, as in the case of the acetaldehyde we found a definite relationship existing between the production of isoacetone (15) and the concentration of the potassium hydroxide used. This analogous enolization of acetaldehyde and isoacetone is shown in the following equations.



The isoacetone molecule should then react in accordance with the following equation.



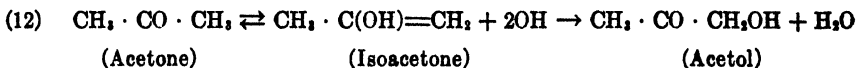
In the presence of an oxidizing agent, acetic acid and formaldehyde would be the products. The formaldehyde would subsequently be converted to carbon dioxide. Dumas and Stas (16), Gottlieb (17), and Herz (18) obtained acetic acid from acetone by using chromic acid as the oxidizing agents. Others have obtained formic and acetic acids by means of silver oxide. Since acetaldehyde is a possible dissociation product of isoacetone, it is clear that vinyl alcohol will form provided the concentration of the base is great enough.

A study of the data obtained in the oxidation of acetone with neutral potassium permanganate will show that there is a sufficient concentration of potassium hydroxide arising from the following reaction



to bring about this vinyl alcohol formation. As shown above this will give rise to oxalic acid and carbon dioxide.

Since Fournier (19) had shown that acetone may be oxidized in part to pyruvic acid with alkaline potassium permanganate, it is obvious that isoacetone, as pointed out by Witzemann (20), must be oxidized to acetol in accordance with the following equation.



That acetone is not oxidized exclusively in alkaline solutions through the intermediate formation of acetol is shown by the fact that acetol differs from acetone in that the amounts of oxalic

and acetic acids obtained from it show certain maxima and minima which acetone does not (21). Finally, it is to be observed that the presence of the alkali exerts a marked effect on the oxidation of isopropyl alcohol as it did in the case of ethyl alcohol i.e., the sensitivity of these compounds to chemical attack is greatly increased by the mass action effect of the added alkali.

THE OXIDATION OF CARBOHYDRATES IN ALKALINE SOLUTION

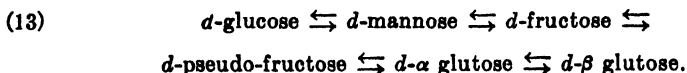
The work described thus far is fairly typical of the experiments which might well be considered as the forerunners of our subsequent studies on the carbohydrates. One of the most outstanding observations which we made in this study of the oxidation of the simpler organic compounds was the marked influence which the alkali normality seemed to have on the general course of a given reaction. In our desire to obtain more data with reference to this effect we turned our attention to the oxidation of the carbohydrates in alkaline solutions.

It is well known that the more common carbohydrates such as glucose, fructose, galactose and sucrose have been oxidized under a great variety of experimental conditions. Many valuable results have been obtained in such work. We were anxious to make a study from the standpoint above noted. In our experiments, certain carbohydrates were oxidized by means of aqueous solutions of potassium permanganate both in the absence and in the presence of varying concentrations of potassium hydroxide. Under these conditions, the carbohydrates chosen were converted exclusively into carbon dioxide, oxalic acid and traces of acetic acid. The general procedures were exactly the same as those used with the compounds of the simpler type. Our average total carbon return was within a few tenths of 100 per cent. From our data we have made the following general observations. (a) *Effect of varying the alkali concentration.* (1) When each of the individual sugars (glucose, mannose, fructose and galactose) which were chosen for our study was oxidized at 25°, 50° and 75°, it was found the amounts of oxalic acid and carbon dioxide formed at a given alkali normality were different. This was especially true at the lower alkalinities. As the concentration of the potassium hydroxide was increased

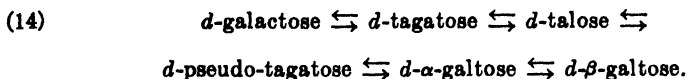
there was a general tendency for the oxalic acid—carbon dioxide ratios to become more nearly the same for all the various temperatures used. (2) At lower normalities of alkali and at a temperature of 50° , the amounts of oxidation products from glucose, mannose and fructose were found to be different for each individual carbohydrate. As the alkali normality was increased, there was a tendency for the amounts of oxalic acid and carbon dioxide from these three hexose sugars to become more nearly the same. At first it was thought that these rather small differences were negligible but our later work showed that they were really differences of some significance. (b) *Effect of temperature.* As the temperature was increased from 50° to 75° , this tendency towards identical values in the amounts of the oxidation products became more marked. At 75° the amounts of oxalic acid and carbon dioxide obtained from glucose and fructose were almost the same. Although we did not study mannose at 75° , yet it will be shown later that it may be predicted with a fair degree of certainty that the amounts of oxalic acid and carbon dioxide obtained from it will be practically the same as that derived from glucose and fructose. Although galactose belongs to another series in the hexose group, namely, galactose, tagatose and talose, yet it was observed that this carbohydrate showed a marked tendency at higher alkali normalities and at higher temperatures to yield oxalic acid and carbon dioxide in amounts which were practically the same as those in our experiments with glucose, fructose and mannose. So much was this the case that we found the data at 75° to be practically identical for glucose and galactose.

These differences and these tendencies toward identical yields of the products obtained in the oxidation of these well known hexose sugars with neutral and alkaline permanganate at different temperatures are very important matters in the chemistry of these compounds. Hence, we turned our attention to the task of finding a reaction mechanism that would account for the facts which we had observed. More especially were we anxious to know whether our data would harmonize with the classical work in the literature of this field. As is well known, the experiments of Lobry de Bruyn and Alberda van Ekenstein (22) concerning

the action of alkalis on aqueous solutions of glucose, mannose and fructose showed that these carbohydrates undergo reciprocal transformations into each other. The equilibrated system formed by the use of either glucose, mannose or fructose is represented by the following equation,

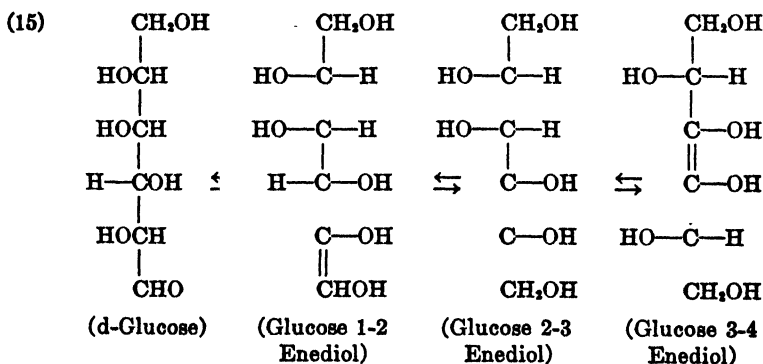


The similar behavior of galactose is shown in the following equation:

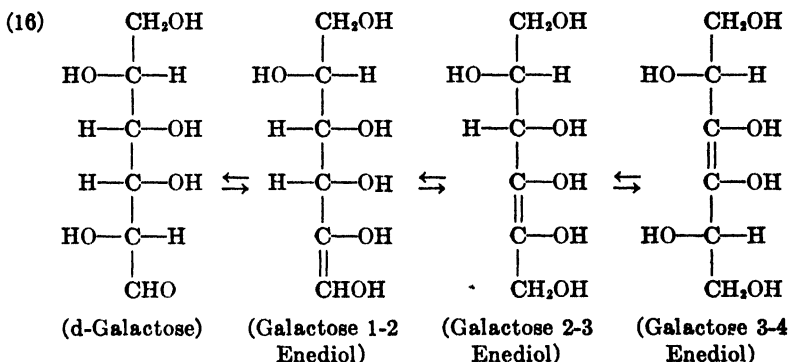


These workers found that glucose, mannose, and fructose did not give rise to equilibrated systems which were quantitatively identical. The same relationship is probably true with reference to the galactose series. This general fact is of extreme importance in understanding the differences and the similarities in the behavior of these hexose sugars under the experimental conditions which we used.

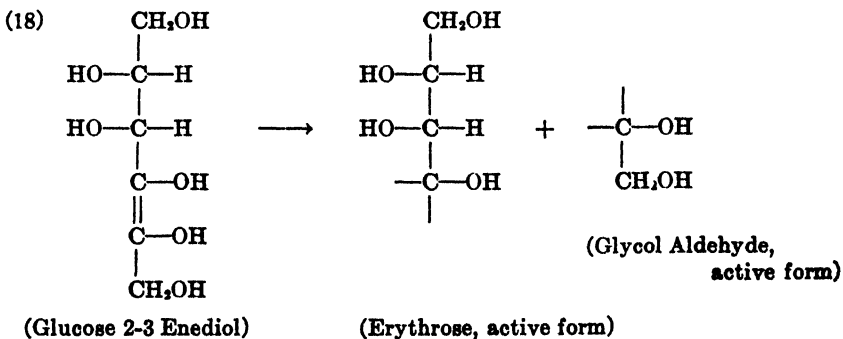
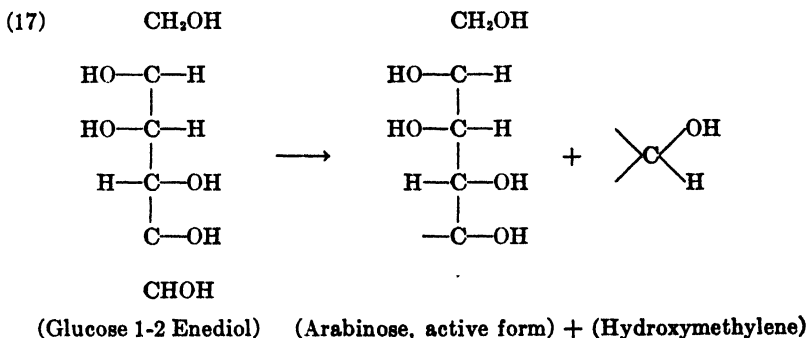
In their study of the behavior of alkalis towards the sugars Nef (23) and his students elaborated the suggestion of Wohl and Neuberg (24) with reference to the existence of a 1-2 enediolic form of glucose. They postulated the presence of two other enediols, namely, the 2-3 and the 3-4 isomers. From the following equation it is clear that mannose and fructose would give rise to exactly the same enediols as glucose.



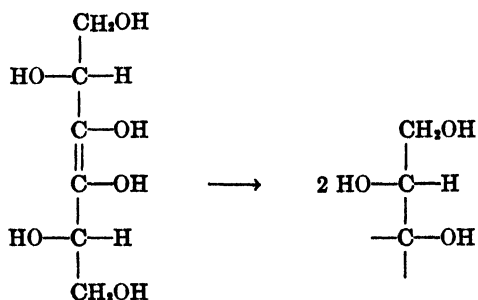
Furthermore, it is equally clear that the enediols of the galactose-tagatose-talose series must be structurally different than the (1-2) and (2-3) isomers from the corresponding ones in the glucose series.



When the double bonds of the several glucose enediols are ruptured the following reactions take place.



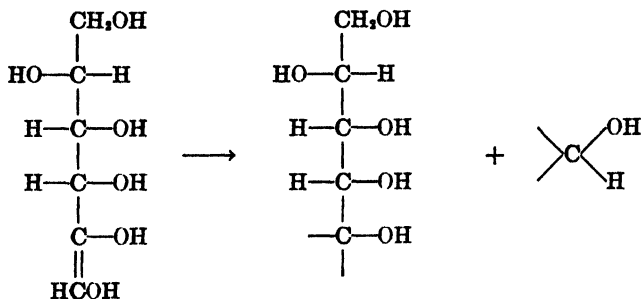
(19)



(Glucose 3-4 Ene diol) (Glyceric aldehyde, active form)

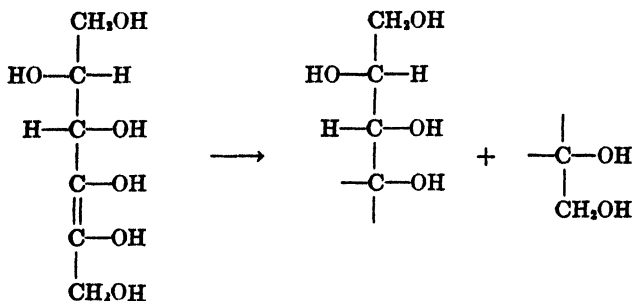
The following reactions take place when the above galactose enediols are ruptured.

(20)



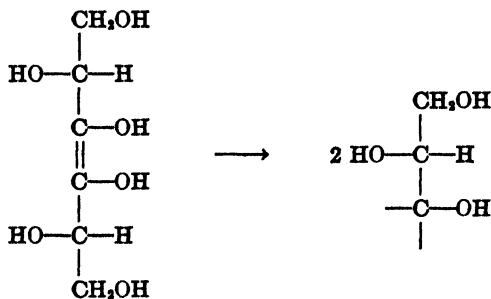
(Galactose 1-2 Ene diol) (Lyxose, active form) (Hydroxymethylene)

(21)



(Galactose 2-3 Ene diol) (Threose, active form) + (Glycolic Aldehyde, active form)

(22)



(Galactose 3-4 Eneidiol)

(Glyceric Aldehyde, active form)

Since mannose and fructose give rise to the same enediols as glucose then it is clear that the qualitative character of the solutions produced through a rupture of these hexose enediols will be the same in each case. The amounts of the fission products should be different in the alkaline solution of these three sugars because of the fact observed by de Bruyn and van Ekenstein namely, that glucose, mannose and fructose did not give equilibrated systems that were quantitatively identical. A rupture of the galactose enediols would result in a system that is chemically different from that formed by the glucose enediols except in the 3-4 enediol. In this case as in all the hexose sugars glyceric aldehyde would be a common component.

It occurred to us (25) that should the equilibrium consisting of the three enediols of a given hexose together with their respective fission products be an integral part of the one observed by de Bruyn and van Ekenstein then there might be certain experimental factors which ought to produce a shifting in such a system. If the alkaline solutions of these carbohydrates give rise to an irreversible equilibrium, then it is probable that the speed of the slowest reaction in the series of changes involved must be influenced by the concentration of the alkali used and the temperature employed. Nef (26) believed that there were no less than 116 substances in these equilibrated mixtures produced by the action of alkalis on the hexose sugars. From the differences and similarities observed in the oxidation products obtained in the glucose-mannose-fructose series, and the relation of the results obtained in the galactose series to those in the

glucose series, it is clear that these experimental factors must undoubtedly be the temperature and the alkali normality.

Sources of the oxidation products. The sources of the reaction products found in these permanganate oxidations and the effect of the variable experimental factors on their amounts may be understood on the basis of these views with reference to the equilibrated condition which is thought to exist in alkaline solutions of these sugars. *Carbon dioxide.* (a) The carbon dioxide obtained in the oxidation of glucose, fructose, mannose, and galactose with potassium permanganate in the absence of any added alkali must come from the ultimate oxidation of hydroxymethylene molecules obtained when the hexose 1-2 enediol undergoes splitting. It is evident that various aldehydes arising from the successive degradation of the hexose through a loss of hydroxymethylene should react in the same manner. We found that arabinose, lyxose and glyceric aldehyde may be oxidized completely to carbon dioxide in the absence of alkali. We had no erythrose or threose available. Our results show a maximum yield of carbon dioxide in those regions of alkalinity where the 1-2 enediol formation is favored. (b) Carbon dioxide may arise from the glycolic aldehyde obtained from the splitting of the *hexose 2-3 enediol*. Nef has shown that the tetroses tend to react as 2-3 enediol and these on splitting would eventually yield more glycolic aldehyde. (c) It has been also shown that glyceric aldehyde in alkaline solution is oxidized in part to carbon dioxide. Hence, the *hexose 3-4 enediol* thus becomes a source of carbon dioxide by reason of its rupture into glyceric aldehyde. *Oxalic acid.* As the alkali concentration is increased the enediolic equilibrium would tend to shift to the region in which the 2-3 hexose enediol predominates. This would tend towards the production of glycol aldehyde, a compound which is oxidized exclusively to oxalic acid and carbon dioxide under our experimental conditions. It was found that the oxalic acid reaches a maximum, after which the yield begins to diminish. This has been thought to be due to the oxalic acid—carbon dioxide ratio in glyceric aldehyde, a fission product of the hexose 3-4 enediol, being of less value than in glycol aldehyde at given alkali normality.

This would mean a tendency in the oxalic acid to approach a minimum. *Acetic acid.* This acid undoubtedly arises from the oxidation of pyruvic aldehyde, pyruvic acid and lactic acid. The sources of these will be discussed below.

Amounts of the oxidation products. The differences in the amounts of the oxidation products in the glucose-mannose-fructose series at the lower alkalinities must be due to a lack of identity in the equilibrium system formed by each individual sugar. As the alkali concentration is increased it is clear that these equilibrated mixtures must shift in each case towards the glucose 3-4 enediol. These alkaline solutions tend therefore to become more nearly identical quantitatively. Hence the amounts of their oxidation products should become more nearly the same. The effect produced by an increase in temperature seems to bring about the same end result. As noted above, the splitting products of the galactose (1-2) and (2-3) enediols are different from those of the glucose series. Hence, quantitative differences in the amounts of oxalic acid and carbon dioxide are rather to be expected. However, the splitting products of the galactose (3-4) enediol are like those of the glucose series. If the increased alkali concentration changes the first splitting products of all hexose enediols into other enediols which in themselves undergo the same fission reaction also, then it becomes clear that the alkaline solutions of all hexose sugars will tend towards identical composition at the higher alkalinities. An added emphasis is given to this point of view when one reflects that all the hexose sugars form a common 3-4 enediol, which, as has been repeatedly stated, will rupture into two molecules of glyceric aldehyde. Whether the saccharines play a part in these reactions has not been established. It is highly probable that the speed of oxidation of the fission products is much greater than that of saccharine formation under these conditions. Hence this factor would have little influence on our results.

ACTION OF POTASSIUM HYDROXIDE ON THE HEXOSES

It now became increasingly important that the alkaline solutions of these carbohydrates should be studied in the absence of

potassium permanganate in order to ascertain whether they would react as though an equilibrated condition was present. This seemed to be the logical procedure because of the obviously important part played by the alkali in our experiments with the simpler types of compounds. We applied the same experimental treatment in this case that we had used in studying the effect of the alkali concentration on the formation of vinyl alcohol from acetaldehyde, and the effect of the same factor on the formation of isoacetone from acetone. The general chemical change taking place in alkaline solutions of these sugars is undoubtedly the same as that in the alkaline solutions of the simpler compounds; i.e., a keto-enol tautomerism, a phenomenon now being studied by W. Lee Lewis and his students in the case of the methylated sugars. We felt that data obtained from experiments involving changing temperature and variable alkalinity ought to shed much light on the validity of our explanation. The brilliant experiments of Nef and his students in this difficult field are well known and in my opinion will stand unchallenged as masterpieces of chemical workmanship. Our procedure consisted in subjecting the carbohydrate under investigation to the influence of variable temperature and changing alkali normality for a definite length of time. The presence of certain reaction products were regarded as evidence for the previous existence of hexose enediolic forms in the alkaline solutions. A consideration of the properties of the various substances which might form in the reaction between potassium hydroxide and these hexose sugars showed that a study of the relationship between the lactic acid yields and the alkali normality would be the most practical method of establishing the presence of an equilibrated system in these carbohydrate solutions. The following will illustrate our plan: *Lactic Acid*: If a hexose (3-4) enediol is ruptured at the double bonds, it should give two molecules of the active form of glyceric aldehyde. This fission product is then converted to pyruvic aldehyde which in turn is changed to lactic acid in alkaline solutions. Hence, *lactic acid* was regarded as an index for the presence of a hexose (3-4) enediol. If the normality of the alkali and temperature are the two factors which influence the status of the general

equilibrated condition in these solutions, then the yields of lactic acid should be functions of these experimental conditions. A comparison of the amounts of lactic acid obtained from glucose, mannose and fructose at 25°, 50° and 75° bears out this point of view (27). It should be emphasized in this connection that the amounts of lactic acid derived from these three well known sugars are practically identical at 75°. These facts are in harmony with the tendency of the oxalic acid-carbon dioxide ratios in the oxidation of fructose and glucose to become more nearly the same at 75° and at the higher alkalinities. Since the amount of lactic acid from alkaline solutions of mannose is practically the same as that from the other two sugars, it is a fair prediction that the oxalic acid carbon-dioxide ratio will also be the same.

Pyruvic aldehyde. If pyruvic aldehyde is a forerunner of lactic acid then the amounts of this compound should also bear a definite relationship to the variable experimental factors employed. This keto-aldehyde was quantitatively determined through its osazone. Our production curves rose to a maximum (28) with an increase in alkalinity and then they receded. These maxima were thought to be points of alkalinity at which the rate of osazone formation was just balanced by that of lactic acid formation. These reactions show a definite temperature coefficient, the maximum point occurring at lower alkalinities with an increase in temperature.

Acetic and formic acids. Acetic acid and a portion of the formic acid may come from the dissociation of pyruvic aldehyde into acetaldehyde and carbon monoxide. These aldehydes are then converted into acetic and formic acids. If a definite hydroxyl ion concentration is necessary to change pyruvic aldehyde into lactic acid, it is obvious that the amounts of acetic and formic acids will tend to diminish in an amount which will be inversely proportional to the amount of lactic acid formed. These maxima in the amounts of acetic and formic acid were found to be present in the alkaline solutions of glucose, mannose, fructose and galactose. Furthermore, we began to find significant yields of lactic acid at approximately those alkali normalities which marked the maxima for acetic and formic acids. This intimate relationship between pyruvic aldehyde, acetic, formic

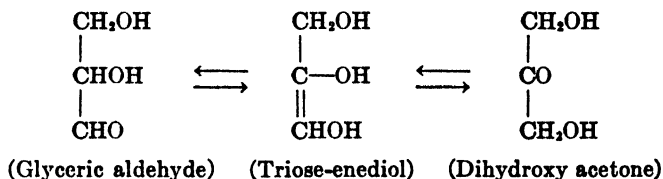
and lactic acid production has been observed in all the hexoses thus far studied. If glyceric aldehyde is the intermediate producing these changes then it follows that all the hexose sugars should react in the same way by reason of the presence of the common hexose (3-4) enediol formation. Formic acid is also regarded as being derived from the splitting of a 1-2 hexose enediol, and also as stated above from a succession of such reactions arising from the residual pentose, tetrose, triose and diose, resulting in each case. The recent paper of Gustus and Lewis (29) on the alkaline oxidation of 2, 3, 4, 6, tetramethyl glucose is an exceedingly important contribution in this field. Glycolic acid would be thought of as an index for the presence of a hexose 2-3 enediol. A precise quantitative method for its determination was not devised since in the glucose-mannose-series the glucose 3-4 enediol seemed to be the favored structure. However, in the galactose series we found that the amounts of galacto-meta-saccharinic acid lactone showed a definite relationship to the alkali normality used. If the increased concentration of the alkali changes the first splitting products of the hexose enediols into other enediols of smaller carbon atom content which will in themselves undergo a further fission reaction then it becomes clear that the alkaline solutions of all the hexose sugars will tend towards an identical composition at the higher alkalinities in the presence of oxidizing agents. These facts account for the greater reducing power observed in carbohydrate solutions as the concentration of the alkali is increased. In his recent important contribution on the copper number of glucose (30) Amick has shown that "the amount of the oxidation is dependent on the alkalinity of the solution." Stieglitz (31) has previously emphasized the fact that "the oxidation of glucose is enormously accelerated in the presence of alkali and it is retarded by the presence of neutralizing acids."

Finally, the experimental results obtained from a study of the behavior of the hexose sugars towards the variable factors of temperature and alkali concentration point strongly to the correctness of the view that a general equilibrated condition is present in these systems and that it may be disturbed by these same factors.

ACTION OF POTASSIUM HYDROXIDE ON THE TRIOSES

It now became necessary to test the validity of the assumption made above with reference to glyceric aldehyde being the forerunner of the lactic acid which was being derived from the alkaline solutions of these hexose sugars. If this assumption is valid then the same relationships which were found to exist between pyruvic aldehyde, lactic, acetic and formic acids in the alkaline solutions of glucose, mannose, fructose and galactose should also be found in alkaline solutions of glyceric aldehyde. Aqueous solutions of equivalent amounts of pure glyceric aldehyde crystals were treated with potassium hydroxide under exactly the same experimental conditions as those used with the sugars themselves (32). Much to our satisfaction *these same general relationships were found to exist in the reaction products of the triose as were found present in the hexoses.*

It should be noted that an equilibrium undoubtedly exists in the alkaline solutions of glyceric aldehyde similar to that observed by de Bruyn and van Ekenstein in the cases of the hexoses. This may be represented by the following equation:



By reason of this possibility dihydroxyacetone (33) was studied in exactly the same manner as glyceric aldehyde had been. Here also we found the same facts with reference to pyruvic aldehyde, lactic, acetic, and formic acids as had been observed in alkaline solutions of glyceric aldehyde. It should be pointed out that lactic acid is the saccharinic acid of the trioses. In connection with the facts represented by the above equation it is to be noted that Fischer, Taube and Baer (34) recently converted glyceric aldehyde to dihydroxyacetone to the extent of 49 per cent.

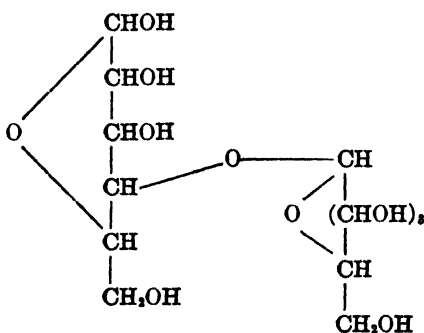
From the relationships here described it seems to follow that the splitting product of a 3-4 hexose enediol, namely, glyceric

aldehyde is responsible for the production of lactic acid in alkaline solutions of glucose, fructose, mannose and galactose.

OXIDATION OF THE POLYSACCHARIDES. ACTION OF POTASSIUM HYDROXIDE ON MALTOS

By reason of the results obtained with the trioses and the hexoses it became of much interest to examine the behavior of certain polysaccharides towards the oxidizing conditions employed throughout this work. We have studied the behavior of lactose, sucrose, maltose, cellose and raffinose towards neutral and alkaline potassium permanganate. Maltose is the only one of these compounds whose action towards aqueous solutions of potassium hydroxide has thus far been examined (35). These solutions were of such a strength that a comparative study could easily be made of the data obtained with our previous work on glucose.

The most recent work in the literature (36) shows that maltose is a 4-glucosido-glucose.



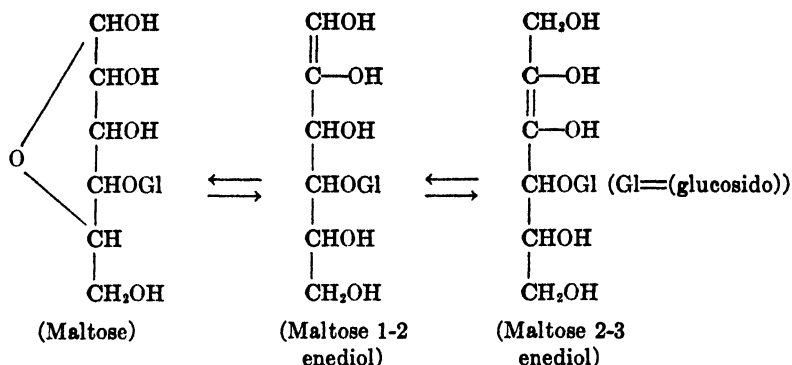
The oxidation products of maltose and of cellose were the same as those obtained with glucose under the same experimental conditions. Our experimental data show two important facts: (a) that the alkali concentration and temperature are the two factors which influence the amount and character of the reaction products; (b) that the first step in the alkaline oxidation of the maltose molecule is not one of a complete hydrolysis of the disaccharide into two molecules of glucose. If such an hydrolysis

had taken place it would naturally follow that the yields of oxalic acid and carbon dioxide would be identical with those of glucose. When maltose and cellose are oxidized at 50° with neutral and alkaline potassium permanganate, the reducing character of the solutions of maltose and cellose are not so great as those of an equivalent solution of glucose at the lower alkalinities and temperature. As the alkali normality is increased the reducing power of the disaccharides is greatly increased. These facts are shown in table 1.

TABLE 1

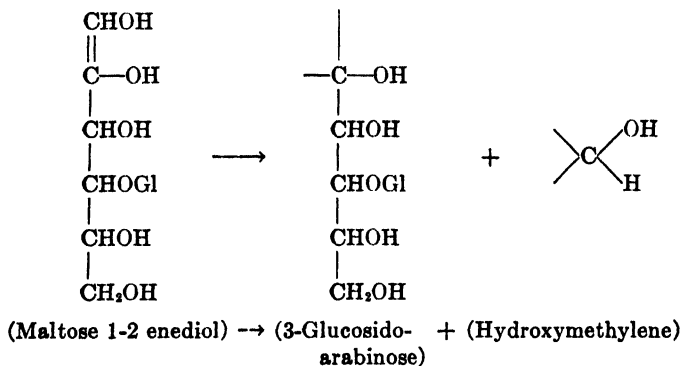
DISACCHARIDE	NORMALITY OF KOH	WEIGHT OF DISACCHARIDE USED	DISACCHARIDE RECOVERED (GLUCOSE)	DISACCHARIDE OXIDIZED (GRAMS)	KMnO ₄ USED BY DISACCHARIDE ACTUALLY OXIDIZED	KMnO ₄ USED BY GLUCOSE EQUIVALENT TO 1.98 GRAMS OF DISACCHARIDE
Maltose.....	0.00	1.98	0.42	1.56	3.84	6.80
	0.05	1.98	0.34	1.64	5.34	8.53
	0.10	1.98	0.34	1.64	6.43	8.53
	0.25	1.98	0.31	1.67	6.80	8.53
	0.50	1.98	0.28	1.70	7.16	8.52
	1.00	1.98	0.25	1.73	7.35	8.53
Cellose.....	0.10	1.98	0.31	1.67	6.43	8.53
	0.25	1.98	0.29	1.69	6.80	8.53
	0.50	1.98	0.26	1.72	7.16	8.52

By reason of these facts a study was next made of the behavior of potassium hydroxide solutions towards maltose in the absence of potassium permanganate to see if the disaccharide would react in response to changes in alkali concentration and also to changes in temperature. This was found to be the case. Therefore *alkaline solutions of maltose must undoubtedly contain an equilibrated condition similar to that observed with the hexose sugars.* The complex components of such a system would be the 4-glucosido-hexose analogues of those compounds observed by de Bruyn and van Ekenstein in the glucose-mannose-fructose series. In addition to these there should be present certain 4-glucosido-glucose enediols (37) and their fission products.

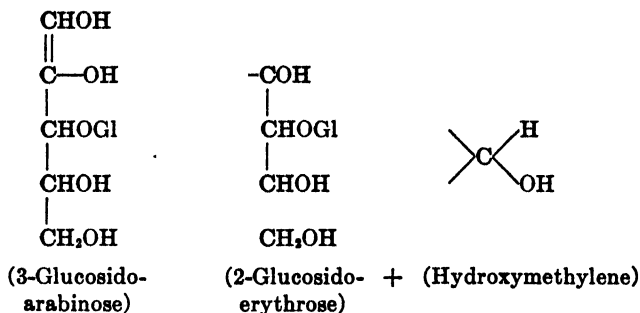


It is obvious that such a system should react to the changing alkali concentration and temperature in quite the same general way as the hexose sugars did.

Maltose 1-2 enediol (4-glucosido-glucose-1-2 enediol). A rupture of maltose 1-2 enediol would result in the formation of hydroxymethylene and 3-glucosido-arabinose according to the following equation.

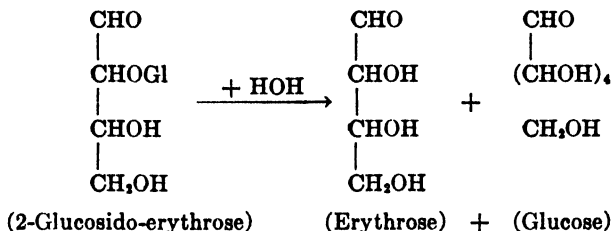


If the CHOGl group does not take part in the enolic changes then it is clear that the 3-glucosido-arabinose may lose an hydroxymethylene group and give 2-glucosido-erythrose as shown in the following equation.



The hydroxymethylene molecules are then converted to formic acid.

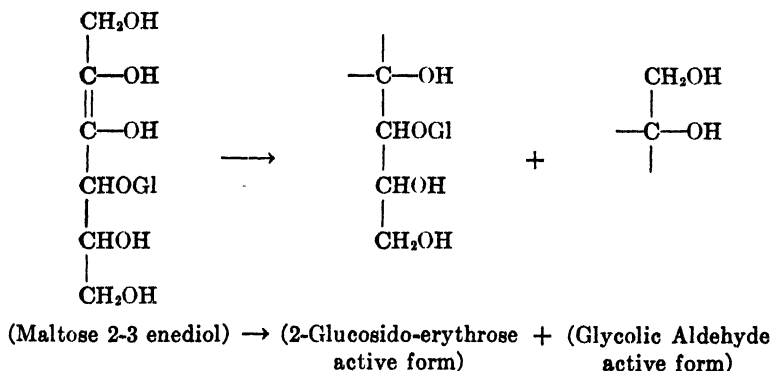
The 2-glucosido-erythrose must now hydrolyze to erythrose and glucose, as shown by the following equation, because it can not further enolize if the CHOGl group remains intact.



Nef (38) believed that tetroses in alkaline solutions reacted as 2-3 enediols, $\text{CH}_2\text{OH} \cdot \text{C}(\text{OH}) = \text{C}(\text{OH}) \cdot \text{CH}_2\text{OH}$, rather than as tetrose 1-2 enediols, $\text{CH}_2\text{OH} \cdot \text{CHOH} \cdot \text{C}(\text{OH}) = \text{CHOH}$. Under these circumstances erythrose could not yield lactic acids because glyceric aldehyde, the forerunner of lactic acid, would not be a fission product of the general reaction. Nef reached this conclusion because he was unable to find the least trace of lactic acid in (8.N) alkaline solutions of glycol aldehyde. However, he did obtain significant amounts of a four carbon atom saccharinic acid (1,3 dihydroxybutyric acid), thus showing that a tetrose had formed from glycolic aldehyde. We confirmed Nef's observation with reference to the presence of lactic acid. We used solutions of less normality. On the other hand Hutchman did succeed in obtaining from alkaline solutions of glycol aldehyde very minute amounts of 1-2 dihydroxybutyric acid and

the 1-3 dihydroxybutyric acid. These were identified through a synthesis of them and through a comparison with specimens kindly furnished to us by Dr. J. W. E. Glattfeld of the University of Chicago. The formation of these two acids seemed to be in harmony with the suggestion made by Miss Marjorie Pickard Benoy and the author with reference to the enediolic forms of the carbohydrates being forerunners of the saccharines. Although our proposed mechanism rests on no experimental basis yet it has aided us in tracing out the compounds which should form in these alkaline solutions.

It is evident therefore that the glucose section of the maltose molecule does not give rise to lactic acid through its action on potassium hydroxide. This follows as a matter of course from the preceding discussion. Obviously the lactic acid obtained from maltose must therefore be a product of the glucosido section which arises from the hydrolysis of the 2-glucosido-erythrose. *Maltose 2-3 enediol* (4-glucosido-glucose 2-3 enediol). As the concentration of the alkali is still further increased the equilibrium will be shifted towards the formation of maltose 2-3 enediol. When the maltose 2-3 enediol undergoes a fission at the double bond, 2-glucosido-erythrose and glycolic aldehyde will be formed as shown by the following equation.



Then it is clear that the 2-glucosido-erythrose will become a source of lactic acid through hydrolysis of the compound into glucose and erythrose as pointed out above.

If the maltose molecule reacts as just outlined, then the yield of lactic acid obtained from the action of aqueous solutions of potassium hydroxide will never be greater than approximately one-half that obtained from glucose. Obviously, the same should also be true for pyruvic aldehyde and acetic acid. Our experimental data show that this is true. Had hydrolysis preceded enolization then our yields of pyruvic aldehyde, lactic and acetic acids should be identical with those obtained from glucose under the same conditions. Glattfeld and Hanke (39) oxidized maltose in alkaline solution with air and also with hydrogen peroxide. On hydrolysis of the glucosido-acids obtained by them as reaction products, they identified d-erythronic lactone and arabonic acid, which was recognized by means of its phenylhydrazide. Another notable fact in this connection was the formation of the C₄ saccharinic acids. All these facts are in harmony with the reactions which have been outlined above for the alkaline decomposition of maltose. A comparison of the data obtained from the oxidation of lactose (40) with those obtained from the oxidation of an equivalent mixture of glucose and galactose shows that the disaccharide is not completely hydrolyzed into its monosaccharide components at the lower alkalinities and temperatures. At the higher alkalinities and higher temperatures our data are practically identical. The same general effect was observed with sucrose (41) and equivalent solutions of fructose and glucose. Raffinose (42) was oxidized and its products compared with the following equivalent solutions; (a) fructose, glucose and galactose; (b) sucrose and galactose; (c) melibiose and fructose.

OXIDATION OF CARBOHYDRATES IN ACID SOLUTION

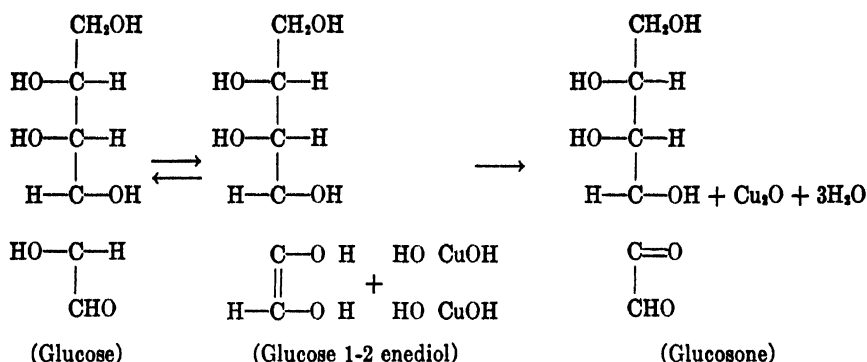
It is evident from the above discussion that the alkali is one of the most important factors having a definite influence in determining the character of the reaction taking place when the carbohydrates and the simpler organic compounds are oxidized in alkaline solutions. Hence, it became of great interest to know whether the reaction mechanism of carbohydrate oxidation in acid solutions could be explained on the principles given above.

In view of the results obtained with the hexose sugars, the question arose whether one or more of these enediols did not exist in solutions of pH value less than 7.

Copper acetate as an oxidizing agent. Copper acetate (43) had previously been used as an oxidizing agent in reactions of this character. It possesses the following distinct advantages; (a) The cupric ion is easily reduced to the cuprous condition and at times metallic copper is also found associated with the cuprous oxide. These facts furnish a ready and an accurate means of calculating the oxygen consumed. (b) The reaction with the hexoses was found to proceed fairly slowly, and could be stopped most easily. (c) Several of the theoretically possible intermediates were known to be stable towards this reagent. Obviously this fact was of extreme value in ascertaining some of the stages through which these oxidations passed. (d) The unused copper ion could be easily removed.

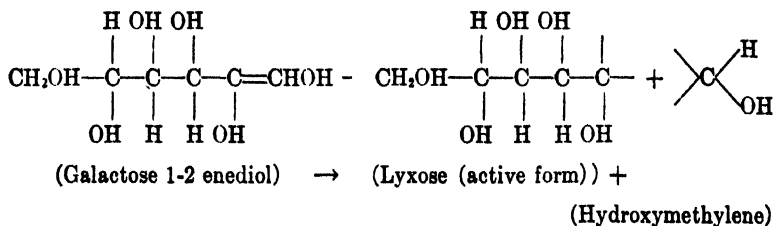
Reaction products. When glucose and fructose were oxidized with copper acetate the reaction mixtures were examined for the following products: formic, oxalic, and glyoxylic acids, carbon dioxide and glucosone. Although not measured quantitatively the presence of glycolic acid was also established. In galactose the same reaction products were obtained save the characteristic hexosone, galactosone. As the hydrogen ion concentration of the reaction mixtures increased the oxidation of glucose and fructose gradually ceased. This fact is one of the most importance when viewed in the light of the discussion above with reference to the function of the alkali (or the hydroxyl ion concentration) in the oxidation.

Reaction mechanism. Glucose and fructose. Owing to the presence of glucosone as one of the reaction products in the oxidation of glucose and fructose with copper acetate solutions, it was concluded that the formation of the hexosone was the first step in the reaction. The formation of gluconic acid from glucose is excluded as an intermediate since it was found that gluconic acid and galactonic acid lactone had no marked effect on aqueous copper acetate solutions. The presence of glucosone is easily understood from the following equations.



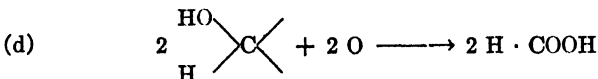
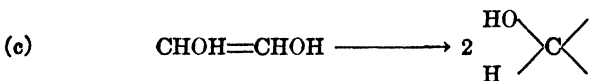
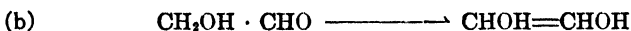
This interpretation would regard the hexose enediol as an acid. Some of the evidence in favor of the acidic character of the carbohydrates is as follows: (a) Michaelis and Rona (44) found the dissociation constant for glucose to be 6.6×10^{-13} , for fructose 8.8×10^{-13} , and for galactose 5.3×10^{-13} . Osaka (45) computed that of glucose to be 5.9×10^{-13} at 25° . Kullgren (46) found that of invert sugar to be 7.2×10^{-13} and that of cane sugar 1.05×10^{-13} at 21° . (b) Powell (47) has shown both by conductivity methods and also by the change of rate in the hydrolysis of ethyl acetate in the presence of fructose and glucose that these carbohydrates form definite compounds with the base, and in the case of sodium hydroxide the reaction takes place in the ratio of one molecule of each. (c) Wolfrom and Lewis (48) found that the pH value of one liter of lime water changed from 12.6 to 10.6 on the addition of one mole of d-glucose.

Formic acid and hydroxymethylene. The 1-2 hexose enediols may suffer a decomposition as is shown for example in the case of galactose in the following equation.



It is clear that the pentose may undergo oxidation to lyxonic acid or it may enolize and split at the double bond in the same manner as the hexose. In our studies thus far carried out, no work has yet been undertaken along this line.

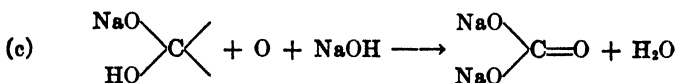
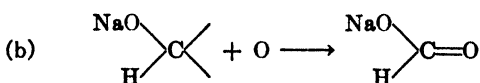
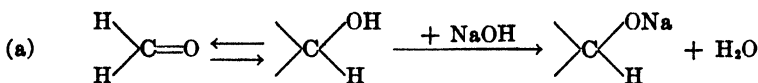
The hydroxymethylene thus formed would be oxidized to formic acid under the conditions of an experiment. In order to experimentally test the assumption that hydroxymethylene, if formed, would undergo an oxidation to formic acid, a study was made of the behavior of hydroxypyruvic acid towards aqueous solution of copper acetate. It was found that this compound was oxidized practically quantitatively to formic acid (95 per cent), and carbon dioxide. The oxygen consumed was found to be 90.5 per cent of that demanded by the use of 2.00 gram atom equivalents. This behavior is easily understood on the basis of the following equations,



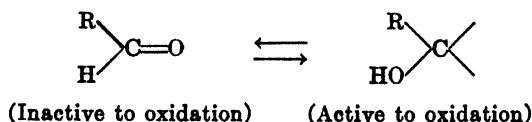
That glycol aldehyde itself will behave towards copper acetate to yield formic acid was shown to be the fact by a separate experiment. This observation is in harmony with that of Heimrod and Levene (49) on the alkaline oxidation of glycol aldehyde with hydrogen peroxide. Hence, in these studies dealing with the mechanism of carbohydrate oxidation hydroxymethylene and its derivatives are considered as active forms of these compounds. In his recent series of lectures at Rice Institute Baly (50) gave expression to the following point of view. "In view of the remarkable reactivity of activated formaldehyde it seems to me necessary to picture a different formula from that given to ordinary formaldehyde. This abnormal activity is well expressed by

the Nef formula, $\begin{array}{c} \text{H} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{OH} \end{array}$, with the carbon bivalent." In 1896 Nef

(51) himself stated that "Die physiologischen Wirkungen des Formaldehyds beruhen zweifellos auf einer Dissociation desselben in Oxymethylen." ("The physiological activities of formaldehyde doubtless depend upon a dissociation of it into oxymethylene.") In this connection it is interesting to observe that McLeod (52) found that formaldehyde and formic acid are unacted upon by copper acetate solutions. Again the important rôle played by alkalis in these oxidations becomes very evident when one examines the behavior of formaldehyde towards oxidizing agents. If hydroxymethylene is formed in these reactions it is clear that it will be oxidized to formic acid. It is a well known fact that formates are oxidized in alkaline solutions to carbon dioxide. The mechanism of this change is easily understood if one considers that the alkali merely causes a shift in the equilibrium expressed by the following equation.

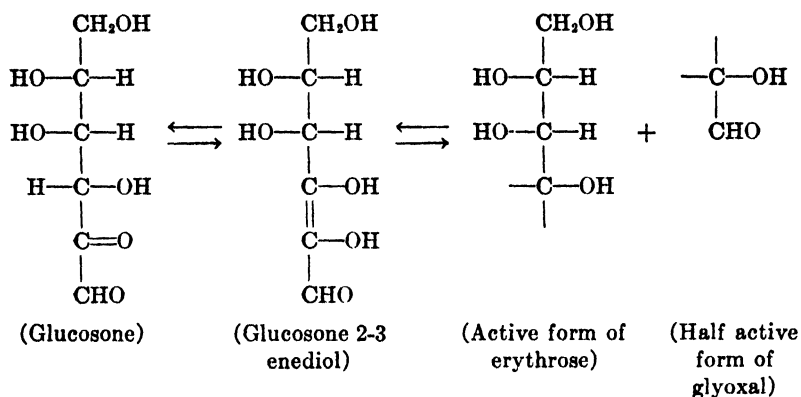


Applying this point of view to the direct oxidation of aldehydes we have the following general reaction,

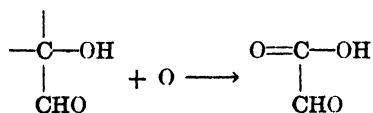


What causes the formation of the active molecules is a problem yet to be solved. *Carbon Dioxide*. The presence of carbon

dioxide in these reactions is thought to be due to the decomposition of the keto-acids. It has been shown above that hydroxypyruvic acid reacts in this manner. *Oxalic, Glyoxylic and Glycolic Acid*. If it is assumed that glucosone and galactosone may also form enediols which will rupture at the double bond in the same manner as in alkaline solutions, then a simple mechanism is available for the reactions producing oxalic, glyoxylic and glycolic acid. The hexosone 2-3 enediol will give rise to the corresponding tetrose and glyoxal in accordance with the following equation.



We did not examine our reaction mixtures for the tetrone acids. However, Morrell and Crofts (53) obtained erythronic acid through the oxidation of glucosone with bromine. The glyoxal (semi-active form) will be oxidized to glyoxylic acid as shown by the following reaction.



The justification for expressing the glyoxal in the active form lies in the experimental fact that specially prepared glyoxal itself does not reduce copper acetate under the conditions of our experiments (50°C). Furthermore, this would seem to be in harmony with the point of view expressed above to the effect that the activated condition of an aldehyde group is best expressed with two valences of the carbon in the unsaturated

condition. In both cases it is strongly suggestive of what has been summed up under the term *nascent*. Debus (54) has shown that glyoxylic acid will rearrange into oxalic acid and glycolic acid. Furthermore he observed that glyoxylic acid does not reduce copper acetate.

CONCLUSION

Finally, it is evident that the molecular stages through which organic compounds pass when they are oxidized in alkaline solutions are largely determined by the normality of the base used. This factor seems to have a marked influence on the status of any equilibrated condition which may be present in any of these oxidation systems. Through a knowledge of theoretically possible intermediates and this latter fact it is possible to account for the presence of a given oxidation product.

In the alkaline oxidation of ethyl alcohol the critical equilibrium is between α -hydroxyethylidene, acetaldehyde and vinyl alcohol; in isopropyl alcohol solutions it lies between isopropylidene, acetone and isoacetone; in the hexose sugars the equilibrated mixture consists of the isomeric hexoses studied by de Bruyn and van Ekenstein and the several enediolic hexose isomers postulated by Nef and their ultimate fission products. These equilibrated systems are markedly disturbed by the magnitude of the alkali concentration and the temperature used.

When these alkaline systems are studied in the absence of an oxidizing agent it is possible to prove experimentally the effect produced by the varying alkali concentration. In the α -hydroxyethylidene-acetaldehyde-vinyl alcohol system the formation of vinyl alcohol is a linear function of the alkali concentration; in the acetone-isoacetone system the concentration of the isoacetone is a logarithmic function of the base used. In alkaline solutions of the hexose sugars and in the disaccharide, maltose, the amounts of lactic acid, pyruvic aldehyde, formic and acetic acids formed are definite functions of the alkali used. The same relationship also holds for the two trioses, glyceric aldehyde and dihydroxyacetone.

In the oxidation of glucose, fructose and galactose in copper

acetate solutions it is possible to trace the reaction mechanism in this acid medium if one assumes an equilibrated condition of certain enediolic forms of the hexose as well as of the hexosone. The tendency of the increased hydrogen ion concentration is to suppress the progress of the oxidation.

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THE INTERIONIC ATTRACTION THEORY OF ELECTRICAL CONDUCTANCE

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I. INTRODUCTION AND DEFINITIONS

The nature of solutions is unquestionably one of the main objects of modern chemistry. It has been customary to define a solution in terms of its concentration. However, it is now a familiar fact that when it is necessary to investigate chemical equilibria such a definition will suffice only when the solutions in question are of such dilution that the ideal gas laws may be utilized to describe the properties of the dissolved substance. For representing deviations from the ideal state the conception of the thermodynamic function called the activity, first defined by G. N. Lewis (1), has proven to be of great importance. It has proven to be of particular value in the study of the marked deviations from ideality which occur in aqueous solutions of strong electrolytes. The idea as developed empirically by Lewis led to the hypothesis (2) that "In dilute solutions of electrolytes the activity coefficient of an ion depends only on the total ionic strength of the solution," the ionic strength of a solution being defined by the expression

$$I = \frac{1}{2} \sum c_i z_i^2 \quad (1)$$

where I = ionic strength.

c_i = concentration in moles per 1000 grams of water.

z_i = valence.

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Brönsted (3) showed, also in an empirical manner, that in the region of sufficiently dilute solutions, in which the behavior of the electrolyte was determined only by its valence type, that in the case of a uni-univalent salt its activity could be expressed by the relation

$$\log f = -3\alpha\sqrt{\gamma} \quad (2)$$

where α = constant dependent on the temperature.

γ = concentration in moles per liter of solution.

In short, the change of the activity coefficient of the ions with concentration in highly dissociated solutions can be represented by a square root law. Equation 2 has more recently been written in a general form which is valid for any valence ion, as follows:

$$\log f = -3\alpha z_i^2 \sqrt{I} \quad (2a)$$

In the limiting case, therefore, the activity coefficient depends only upon the square root of the ionic strength and the valence of the ion in question.

The interionic attraction theory of activity, first developed by Milner (4), and later in simpler form by Debye and Hückel and by Debye (5), gives an adequate theoretical explanation of these empirical laws, based on the fact that the thickness of the ionic atmosphere of mean charge surrounding each ion has to be proportional to the square root of the concentration, if the principal forces between ions are the ordinary Coulomb forces.

However, it is not the purpose of this article to treat the activity problem;³ rather it is its purpose to show in the first part how these fundamental ideas have been applied by Debye and his co-workers to show that the square-root law, found experimentally by Kohlrausch, is the correct one to explain the change in electrical conductance of dilute solutions of electrolytes with

³ The activity problem has been the subject of a number of reviews. The following articles may be mentioned in this connection:

Brönsted: *Trans. Faraday Soc. Symposium on Strong Electrolytes*, April, 1927.

Hückel: *Ergebnisse d. exakt. Naturwiss.* III, 199 (1924).

LaMer: *Trans. Am. Electrochem. Soc.* **41**, 507 (1927).

Noyes: *J. Am. Chem. Soc.* **46**, 1080, 1098 (1924).

concentration, and in the second part, to show how these ideas have led to the prediction of an electrical conductance which is dependent on the frequency used to measure it.

Definitions

In treating the quantitative problem of the electrical conductance of solutions of strong electrolytes it is necessary to define carefully a number of quantities. For the elementary quantities (in electrostatic units), specific conductance, molar conductance, and equivalent conductance the symbols, λ , Λ , and Λ^* , respectively, will be used. Further, the molecular concentration and equivalent concentration are given by the symbols γ and γ^* , respectively. According to the familiar definitions of physical chemistry,

$$\Lambda = \frac{1000 \lambda}{\gamma}; \Lambda^* = \frac{1000 \lambda}{\gamma^*} \quad (3)$$

Also,

$$\gamma = \gamma^* m \quad (4)$$

where m is the valence factor defined for a given ion by the relation

$$m = \nu_i z_i$$

where ν_i is the number of ions formed from one molecule.

Therefore the relation between molar conductance and equivalent conductance is

$$\Lambda^* = \frac{\Lambda}{m} \quad (5)$$

It is customary in physical chemistry to use the practical system of units, i.e., for $\bar{\Lambda}$ the unit OHM⁻¹ CM². In this article the quantities which are given in practical units are designated by a bar over the symbol which represents the quantity in question, thus

$$\bar{\Lambda} = \frac{\Lambda}{9 \times 10^{11}} \quad (6)$$

The mobility of an ion of the i^{th} kind will be designated by the symbol \bar{L}_i . If a molecule is dissociated into ions of the number $\nu_1 \dots \nu_i \dots \nu_s$, of charge $e_1 \dots e_i \dots e_s$, with valences $z_1 \dots z_i \dots z_s$ and friction coefficients $\rho_1 \dots \rho_i \dots \rho_s$, then the molecular conductance at infinite dilution is written

$$\bar{\Lambda}_\infty = \sum \nu_i \bar{L}_i \quad (7)$$

$$\text{where } \bar{L}_i = \frac{N\epsilon^2}{9 \times 10^{11} \rho_i} z_i^2$$

$$N = 6.06 \times 10^{23}$$

$$\epsilon = 4.774 \times 10^{-10} \text{ e.s.u.}$$

Between the mobilities, \bar{L}_i and the friction coefficients, ρ_i there exists the relation

$$\bar{L}_i = \frac{15.34}{\rho_i} z_i^2 \times 10^{-9} \quad (8)$$

The mobilities, \bar{L}_i , used in this article are related to the mobilities usually found in tables of physical constants, \bar{l}_i , by the simple relation

$$\bar{L}_i = z_i \bar{l}_i \quad (9)$$

Further, the ionic strength to be used in this article is the one defined by Bjerrum rather than the Lewis quantity referred to above. This ionic strength is given by the equation

$$I = \sum \gamma_i z_i^2 \quad (10)$$

A purely arbitrary method of referring to electrolytes of the various valence types has been adopted. Those electrolytes which give two different kinds of ions are called *simple* electrolytes. The simple electrolytes are further subdivided into *symmetrical* and *unsymmetrical* electrolytes depending on whether the ions formed have equal or unequal valences. Thus an electrolyte of the type 1-1 or 2-2 is said to be symmetrical, while one of the type 1-2 or 2-3 is unsymmetrical.

II. THE LIMITING LAW OF THE ELECTRICAL CONDUCTANCE OF SOLUTIONS OF STRONG ELECTROLYTES. STATIONARY CASE

As the fundamental ideas underlying the treatment of the conductance problem are the same as those mentioned for the treatment of the activity problem, it is well to consider them in some detail at this point. In the first place Coulomb's law as used here, i.e., to measure the forces between the ions, states that these forces are inversely proportional to the square of the distance between them. As a result of the presence of these Coulomb forces a completely random distribution of ions in an electrolyte solution is impossible. The probability that two oppositely charged ions will come near to each other is greater than the probability that like charged ions will find themselves in the same position. To describe these deviations from a random arrangement of ions the conception of an "ionic atmosphere" has been introduced. This ionic atmosphere may be conveniently described in terms of two of its characteristic properties, 1, its thickness and 2, its time of relaxation.

1. Thickness, $\frac{1}{\kappa}$

If a straight line of length r , is considered with a given ion attached to one end and an element of volume at the other, it is found that sometimes there is an excess of positive and at other times an excess of negative electricity in the element of volume. The time integral of this charge divided by the time of observation gives its mean charge. The density of the ionic atmosphere is the mean charge divided by the volume of the element. The density in the ionic atmosphere is of opposite sign to the charge carried by the ion, and decreases as the length r is increased. It is possible to show that the significant factor in representing this decrease in density with distance is the exponential $e^{-\kappa r}$, where κ has the dimension of a reciprocal length and is given by the formula

$$\kappa^2 = \frac{4\pi}{DkT} \sum n_i e_i^2 \quad (11)$$

Where D = dielectric constant of the solvent

k = Boltzmann's constant = 1.372×10^{-16} erg/degree.

T = absolute temperature

N_i = number of ions of the i^{th} kind in 1 cc.

e_i = charge on ion of the i^{th} kind.

The order of magnitude of κ in centimeters is

$$\frac{1}{\kappa} = \frac{10^{-8}}{\sqrt{\gamma}} \text{ cm.} \quad (12)$$

where γ is the concentration in moles per liter. It is further suggested by table 1 which gives the values of the thickness $\frac{1}{\kappa}$ in centimeters for $\gamma = 0.001$ in water at 18°C.

TABLE 1

TYPE OF ELECTROLYTE	THICKNESS
	cm.
1-1	96.6×10^{-8}
1-2	55.9×10^{-8}
2-2	48.3×10^{-8}
1-3	39.5×10^{-8}
1-4	30.7×10^{-8}
2-4	27.8×10^{-8}

The characteristic dependence of the thickness on the concentration $\gamma^{\frac{1}{2}}$, is explanation for the fact of the proportionality of the change of the logarithm of the activity coefficient with the square root of the concentration and therefore with the square root of the ionic strength, the latter containing both a concentration and valence term. As will be seen it is also explanation for the law of conductance found by Kohlrausch.

2. Time of relaxation, θ

The influence of this property of the ionic atmosphere is extremely important in the consideration of the irreversible process of conduction. The ionic atmosphere can neither be destroyed nor created in an infinitely small period of time. If an ion is

suddenly separated from the solution, the regularity in its neighborhood will cease to exist because it owes its presence only to the force field of the central ion. The transfer to the regular orientation with reference to the point where the ion was will take place gradually. The time necessary for this change is the time of relaxation, and is dependent on a number of factors. It is dependent on the quantities which characterize the thickness of the ionic atmosphere, also it is dependent on the mobility of the ions. Its order of magnitude in seconds has been shown to be

$$\theta = \frac{10^{-10}}{\gamma} \text{ seconds} \quad (13)$$

TABLE 2

ELECTROLYTE	TIME OF RELAXATION	CORRESPOND- ING WAVE LENGTHS
	<i>seconds</i>	<i>meters</i>
KCl.....	0.553×10^{-7}	16.6
HCl.....	$.189 \times 10^{-7}$	5.67
MgCl ₂	$.324 \times 10^{-7}$	9.72
CdSO ₄	$.315 \times 10^{-7}$	9.45
LaCl ₃	$.162 \times 10^{-7}$	4.86

The values of θ for $\gamma = 0.001$ in water at 18°C. for several electrolytes are given in table 2. There have also been included in this table corresponding wave lengths whose significance will be recognized in Part III.

In the following pages it will be shown that the dissymmetry of the ionic atmosphere caused by this time of relaxation, though small, is sufficient to cause an additional (resisting) force on an ion as it passes through the solution. This force is appreciable because of the relatively large value of the charge carried by an ion.

According to present views electrical conductance in solutions of electrolytes is explained in the following manner. Due to the influence of the outer electric field each ion, because of its charge, is subjected to a force. This force gives to the ion a velocity which is proportional to this force. Its velocity is also

dependent upon the forces which resist the passage of the ions through the solution, namely, the frictional forces; but these may be neglected for the moment. At this point we shall consider only the velocity which the ion assumes under the influence of the outer electric field at infinite dilution. The resulting electrical force E_i is proportional to this field-strength because otherwise Ohm's law would not be obeyed. If $z_i e$ is the charge of the ion and X the outer field-strength then

$$E_i = z_i e X = \rho_i v_{i\infty} \quad (14)$$

where ρ_i specifies that outer electric force which gives to the ion a velocity of 1 cm. per second, and $\rho_i v_{i\infty}$ is a measure of the resisting forces which the ion meets when it moves with the velocity $v_{i\infty}$ under the influence of the outer field strength X .

At finite concentrations equation 14 is no longer strictly obeyed, since it fails to take into account the forces of relaxation and electrophoresis which are about to be discussed. The absolute value of the velocity which an ion has under the influence of a unit outer field is called its mobility, u_i . This mobility u_i is related to the mobility \bar{l}_i in the following manner:

$$\bar{u}_i = \frac{1}{96500} u_i$$

$$\bar{l}_i = 96,500 \bar{u}_i.$$

$$u_i = \frac{|v_i|}{X} \text{ (absolute electrostatic units)} \quad (15)$$

The connection between electrical field-strength and current density follows directly. If a molecule of the salt is dissociated on solution into ions $\nu_1 \dots \nu_i \dots \nu_s$, with valences $z_1 \dots z_i \dots z_s$, number present per cubic centimeter $n_1 \dots n_i \dots n_s$, and quantities $\rho_1 \dots \rho_i \dots \rho_s$, which measure the resisting forces of the passage of the ions, then the current density j (current strength per square centimeter cross-section) is given by the expression

$$\begin{aligned} j &= e \sum n_i z_i v_i \\ &= e \sum n_i |z_i| u_i X \end{aligned} \quad (16)$$

The specific conductance λ is defined as the current density for unit field-strength. Therefore,

$$\lambda = \frac{j}{X} = e \sum n_i |z_i| u_i \quad (17)$$

From formula (17) the expression for the specific conductance at infinite dilution can now be written

$$\lambda_{\infty} = e^2 \sum \frac{n_i z_i^2}{\rho_i} \quad (17,a)$$

For finite concentrations the mobilities u_i are necessary to calculate the specific conductance, or any of the conductances derived from it, again using equation 17.

It is evident that there are two possible methods in which the change of conductance with concentration may be explained, as follows:

First, the number of ions n_i may be considered to be variable. This is the method of the classical theory in which a thermodynamic equilibrium between undissociated molecules and the dissociated ions is assumed. The method of treatment is that by which the number n_i is decreased by multiplication by a factor α , the "degree of dissociation," as the concentration increases. This is familiar as the classical theory and will not be discussed further.

Second, the conductance may change with concentration because of variations in the mobilities, u_i . This possibility involves the assumption of complete dissociation, or that the number of ions n_i is always exactly proportional to the total concentration. This assumption is the one which had to be made in the treatment of the activity problem; furthermore it is the one which is used by Debye and Hückel to explain the deviations of the proportionality between the conductance and concentration and which is used throughout the work reviewed in this article.

When an outer field-strength is applied to a solution of finite concentration each ion will no longer move with the same velocity as it did in the infinitely dilute solution because now other forces

between the ions come into play, since each ion finds itself in the presence of others. In other words, the mobility u_i at finite concentration will differ from that at infinite dilution $u_{i\infty}$. In the first place the distribution of the ions in the solution is such that on the average in the neighborhood of an ion of given sign there are more ions of unlike than of like sign. Each ion is surrounded by an ionic atmosphere, the properties of which have been suggested above. This ionic atmosphere is built symmetrically about a stationary ion, but if the ion is caused to move through the liquid with the velocity v , the ionic atmosphere about it can no longer be symmetrical. It is true that the interionic forces tend to restore the symmetry of the ionic atmosphere, but as has been shown, this requires a definite period of time—the time of relaxation. Since the ion is moving, the symmetry of the ionic atmosphere is never completely restored; however, there will be built about each moving ion a stationary ionic atmosphere which moves with the ion to which it belongs. This ionic atmosphere will be unsymmetrical in the direction of the motion of the ion. Before the ion there will be more ions of like charge and behind it more ions of opposite charge than was the case when the ion was not moving. The electrical forces will not be able to build up the static ionic atmosphere before the ion, while a definite period of time is necessary to restore the ionic atmosphere behind it. This granted, it is evident that each moving ion, positive or negative, is subjected to a force which decreases its mobility, since bodies charged alike repel each other and bodies charged unlike attract each other. This force will be called the electrical force of relaxation in the sections to follow.

As a result of the characteristic properties of the ionic atmosphere this electrical force of relaxation is dependent on a number of circumstances. In the first place, the greater the velocity of the ion the greater the additional electrical force will be, because the ionic atmosphere will deviate more and more from that of the stationary case, at least for small velocities. If the friction constants of the ions ρ_i are larger the electrical forces of relaxation are increased because the adjustment of the ionic atmosphere is more difficult. If the temperature is decreased, the electrical

forces of relaxation are again increased, again because the adjustment of the ionic atmosphere is more difficult. In short, the mobility is modified by the ionic atmosphere. Therefore, the ionic atmosphere with its characteristic thickness, which is also a function of the (ionic) concentration plays a very important part in the determination of the magnitude of this force which resists the passage of an ion (6). The problems which confronted Debye and Hückel at this point were, first, to find an expression for the space distribution of ions, taking into account its variation with time, and second, to calculate the stationary dissymmetry around an ion moving with a constant velocity v in the direction of the external field. Their solution, the details of which are given in the original article, was found in the general equations which describe the Brownian movement, and leads to the result that the passage of an ion through the solution is subjected to an additional electrical force of relaxation, E'_i , in the direction opposite to its velocity,

$$E'_i = -\frac{1}{2} \frac{\rho v_i}{DkT} \kappa \epsilon^2 z_i^2 \quad (18)$$

where the mean friction constant of the solution $\rho = \frac{\sum n_i \epsilon_i^2 \rho_i}{\sum n_i \epsilon_i^2}$

Thus, if only the electrical forces acting on an ion are considered the total force is the algebraic sum of the two which have been evaluated.

$$E = E_i + E'_i = z_i \epsilon X - \frac{1}{2} \frac{\rho v_i}{DkT} \kappa \epsilon^2 z_i^2 \quad (19)$$

For a steady state of motion these electrical forces must be in equilibrium with other forces. These other forces are frictional in nature as has already been suggested in equation (14)

$$F_i = \rho_i v_i$$

which expresses the frictional force on the ions exerted by the impacts of the surrounding molecules. The force may also be expressed in terms of Stokes law as follows:

$$F_i = 6 \pi \eta b_i v \quad (20)$$

where η is the internal friction constant of the liquid. In a solution of finite concentration the apparent frictional constant will vary from the limiting value, ρ_i , again because of the distribution of ions about the one in question. In such a solution all the positive ions are moving towards the cathode, while all the negative ions are moving in the opposite direction. But in the vicinity of a given ion there are on the average more ions of unlike than of like sign. Since the ions carry with them a certain amount of the solvent the given ion may be considered to be moving in a medium that is moving in a direction opposite to its motion rather than in a stationary medium, so that a decrease in the mobility results from this force. This effect is the simple electrophoretic effect, and is calculated in a manner similar to that utilized by Helmholtz in earlier studies of this phenomenon. The electrophoretic effect was shown by Debye and Hückel to be given by the expression

$$F_i^1 = e z_i \kappa b_i X \quad (21)$$

where b_i is the radius of the ion of the i^{th} kind.

Therefore the purely frictional forces are given by the algebraic sum

$$F = F_i + F_i^1 = \rho_i v_i + e z_i \kappa b_i X \quad (22)$$

As already indicated, for a steady state of motion the two sets of forces must be in equilibrium

Therefore,

$$E_i + E_i' = F_i + F_i',$$

That is,

$$e z_i X - \frac{1}{2} \frac{\rho v_i}{DkT} \kappa e^2 z_i^2 = \rho_i v_i + e z_i \kappa b_i X$$

or

$$v_i = e z_i X \cdot \frac{1 - \kappa b_i}{\rho_i + \frac{1}{2} \frac{\rho}{DkT} e^2 z_i^2 \kappa} \quad (23)$$

For the mobility u_i this equation may be written

$$u_i = \frac{v_i}{X} = u_{i\infty} \left[1 - \left(\frac{1}{2} \frac{\rho}{\rho_i} \frac{e^2 z_i^2}{DkT} + b_i \right) \kappa \right] \quad (24)$$

where

$$u_{i\infty} = \frac{e z_i}{\rho_i}$$

Thus, in the region of small concentration the mobility is proportional to the square root of the concentration, since the factor κ is proportional to this quantity. Thus the law found empirically by Kohlrausch is explained.

From this expression others giving the molar conductance, the equivalent conductance, and the so-called conductance coefficient of Bjerrum (7) may be written. For example, the molar conductance of a simple electrolyte in sufficiently dilute solution may be given by an expression of the form

$$\Lambda = \Lambda_\infty - \Lambda_\infty \left[\frac{K_1}{D^{\frac{1}{2}}} w_1 + \frac{K_2}{D^{\frac{1}{2}}} b \right] \sqrt{2} \gamma \quad (25)$$

where K_1 and K_2 are constants varying only with the temperature,

$$w_1 = \frac{1}{2} \left(\frac{u_{1\infty}}{u_{2\infty}} + \frac{u_{2\infty}}{u_{1\infty}} \right)$$

$u_{1\infty}$ $u_{2\infty}$ = mobilities of anion and cation

b = harmonic mean of the ionic radii

and γ = molecular concentration

It may be further simplified to

$$\Lambda = \Lambda_\infty - \alpha \sqrt{\gamma} \quad (25,a)$$

where α = numerical factor.

Debye and Hückel tested this equation by making a survey of the existing conductance data for dilute aqueous solutions. They found in practically every case the linear relation between the equivalent conductance and the square-root of the concentration demanded by the equation. It is, as suggested above, in

exactly the form of the expression found empirically by Kohlrausch to hold for very dilute aqueous solutions.

The experimental verification of the equation in non-aqueous solutions is more difficult for several reasons of which the following may be mentioned.

1. The experimental data are incomplete, and in a number of cases where they have been reported they must be considered as unreliable.

2. Since the theory is applicable only when the electrolyte in solution is completely dissociated, measurements in non-aqueous solutions have to be made at greater dilutions even than in the case of the aqueous solutions. In non-aqueous solvents the presence of undissociated molecules even in dilute solutions is a much more common phenomenon than in water. It goes without saying then, that the experimental difficulties may become very great.

In spite of these difficulties Fraser and Hartley (8) have shown that the square-root law is satisfied by the conductance data for a number of uni-univalent salts dissolved in methyl alcohol up to a concentration of $\gamma = 0.002$. These experiments were conducted with extreme care and the results must be considered to be among the most accurate conductance data available at the present time. Walden, Ulich and Busch (9) tested the theoretical relation with their data, and found it to be obeyed for a number of salts dissolved in acetone up to a concentration of $\gamma = 0.0005$. In the more dilute solutions the data of Franklin and Kraus (10) and of Kraus and Bishop (11) for certain of the alkali-halides dissolved in liquid ammonia may be represented by the equation given above.

The development of the theory by Onsager

To this point the numerical factor α in equation (25a) has not been considered. Unfortunately the equations lead to a numerical factor which is more complicated than the corresponding factor in the activity theory which is made up of universal constants only. The factor of the conductance equation has to be calculated for each individual case from the conductance measurements

themselves, because one of the terms from which it is obtained contains the ionic radius—a distance not accurately known at present. Also, if this distance is calculated from the mobility of the ion, using Stokes Law, and the result used to calculate α it is found that the calculated decrease in conductance as the concentration is increased is always somewhat large.

On investigation of these difficulties Onsager (12) was able to improve the theory in several respects. In the first place he was able to calculate the effect due to electrophoresis in such a way that in the region of small concentrations it was entirely independent of the ionic radius. The result is given by the expression

$$F'_i = \frac{e z_i X \kappa}{6 \pi \eta} \quad (26)$$

This expression is essentially the one found previously by Debye and Hückel (equation 21), since it may be obtained from the latter by the simple substitution of the equivalent of the ionic radius given by Stokes Law. Therefore, although the calculation of the factor α was simplified in this manner, the difficulty concerning its magnitude was not removed.

Onsager showed further that the method used by Debye and Hückel to calculate the electrical force of relaxation upon an ion passing through a solution needed some modification. The original Debye expression

$$E'_i = - \frac{1}{2} \frac{\rho v_i}{DkT} \kappa e^2 z_i^2 \quad (18)$$

was obtained by considering the ion to be moved in a given direction with a constant velocity, which, according to Onsager, cannot be strictly true. The ion, in addition to its mean motion in the given direction, possesses an irregular motion, due to its Brownian movement, which will have an effect on the dissymmetry of the ionic atmosphere. Introducing this conception it is found that the resistance to the passage of an ion is lower than was indicated by the earlier treatment. The calculation is also modified due to the fact that the diffusion of two ions in relation to one another causes a combined relaxation of both ionic atmos-

pheres. The additional electrical force of relaxation is calculated to be

$$E_i'' = \frac{e^2}{3 DkT} \frac{\kappa'^2}{\kappa + \kappa'} X \quad (27)$$

where

$$\kappa'^2 = \frac{4 \pi}{DkT} \frac{\sum \frac{n_i e^2}{\rho_i}}{\sum \frac{1}{\rho_i}}$$

n_i and ρ_i being the number and frictional coefficients, respectively of the various ions in the solution, as before.

The result of the calculations of Onsager may be given quite simply by means of the relation

$$\bar{\Lambda} = \bar{\Lambda}_\infty - \bar{\Lambda}_{I0} - \bar{\Lambda}_{II} \quad (28)$$

where Λ_∞ = ordinary conductance at infinite dilution

$$\bar{\Lambda}_{I0} = \frac{|e_1 e_2|}{3 DkT} \kappa \bar{\Lambda}_\infty \frac{q}{1 + \sqrt{q}} = \text{electrical force of relaxation expressed as conductance.} \quad (28,a)$$

$$\bar{\Lambda}_{II} = \frac{n_1 e_1^2 + n_2 e_2^2}{6 \pi \eta} \frac{1000}{\gamma} \frac{1}{9 \times 10^{11}} \cdot \kappa = \text{electrophoretic force expressed as conductance.} \quad (28,b)$$

$$\kappa^2 = \frac{4 \pi e^2 N}{DkT} \frac{1}{1000} \gamma \sum v_i z_i^2 \quad (28,c)$$

For water at 18°C.:

$$\kappa^2 = 0.05342 \times 10^{16} \gamma \sum v_i z_i^2$$

For water at 25°C.:

$$\kappa^2 = 0.05385 \times 10^{16} \gamma \sum v_i z_i^2$$

Equation 28 shows at a glance that the molecular conductance, $\bar{\Lambda}$, is equal to the familiar molecular conductance at infinite dilution, $\bar{\Lambda}_\infty$, minus the effect of the two additional forces, which have been under discussion, namely the electrical force of relaxa-

tion and the force due to electrophoresis. These forces are, of course, expressed as molecular conductances.

The quantity, q , depends only on the valences and mobilities. It is given by the relation

$$q = \frac{\bar{L}_1 z_2 + \bar{L}_2 z_1}{(z_1 + z_2) (\bar{L}_1 z_1^2 + \bar{L}_2 z_2^2)} z_1 z_2 \quad (29)$$

Introducing the universal constants the expression for the molecular conductance of a simple electrolyte takes the following form

$$\bar{\Lambda} = \bar{\Lambda}_\infty - \left(\frac{0.985 \times 10^6}{(DT)^{\frac{1}{2}}} w \bar{\Lambda}_\infty \sqrt{\sum v_i z_i^2} + \frac{29.0}{(DT)^{\frac{1}{2}} \eta} (\sqrt{\sum v_i z_i^2})^3 \right) \sqrt{\gamma} \quad (30)$$

where

$$w = \frac{2q}{1 + \sqrt{q}}$$

The molar conductance, $\bar{\Lambda}$, is therefore given by an expression of the form

$$\bar{\Lambda} = \bar{\Lambda}_\infty - \alpha \sqrt{\gamma} \quad (30a)$$

where

$$\alpha = \left(\frac{0.985 \times 10^6}{(DT)^{\frac{1}{2}}} w \bar{\Lambda}_\infty \sqrt{\sum v_i z_i^2} + \frac{29.0}{(DT)^{\frac{1}{2}} \eta} (\sqrt{\sum v_i z_i^2})^3 \right)$$

The corresponding expression for the equivalent conductance (the quantity used exclusively by Onsager) is

$$\bar{\Lambda}^* = \bar{\Lambda}_\infty^* - \left(\frac{0.985 \times 10^6}{(DT)^{\frac{1}{2}}} w \bar{\Lambda}_\infty^* + \frac{29.0 (z_1 + z_2)}{(DT)^{\frac{1}{2}} \eta} \right) \sqrt{(z_1 + z_2) \gamma^*} \quad (31)$$

This equation is of the form

$$\bar{\Lambda}^* = \bar{\Lambda}_\infty^* - \alpha^* \sqrt{(z_1 + z_2) \gamma^*} \quad (31a)$$

where

$$\alpha^* = \frac{0.985 \times 10^6}{(DT)^{\frac{1}{2}}} w \bar{\Lambda}_\infty^* + \frac{29.0 (z_1 + z_2)}{(DT)^{\frac{1}{2}} \eta}$$

The limiting law for the equivalent conductance may be written in still simpler form when the ionic strength, I' , given by equation 10, is introduced. It may be written

$$\bar{\Lambda}^* = \bar{\Lambda}_\infty^* - \alpha^* \sqrt{I'} \quad (32)$$

where α^* has the value given above.

The above general equations contain, besides universal constants, only the valences of the ions in question and their velocities of migration at infinite dilution. According to these equations, the decrease in conductance with increasing concentration takes place more rapidly the higher the valences are, and the greater the ionic mobilities at infinite dilution are. The valence effect predominates because it occurs in both members of the term which gives the numerical factor.

Considerable progress has already been made in the verification of the theory.

For solvent water at 18°C., using the values of Drude for the dielectric constant of water

$$\alpha^* = 0.270 w \bar{\Lambda}_\infty^* + 17.85 (z_a + z_c)$$

For solvent water at 25°C.

$$\alpha^* = 0.274 w \bar{\Lambda}_\infty^* + 21.14 (z_a + z_c)$$

That the experimental data of Kohlrausch (13) for salts of the valence types 1-1, and 1-2, as well as for acids of the type 1-1 may be represented by the equation of Onsager is indicated in tables 3 and 4. In practically every case the deviations are within the limit of the experimental error. The fact that the differences between experiment and theory are somewhat greater in the case of the uni-bivalent salts is explained by the fact that only five values of the molar conductance, corresponding to the concentrations $\gamma^* = 0.0001, 0.0002, 0.0005, 0.001$, and 0.002 could be used. In the case of the uni-univalent salts the concentrations used were $\gamma^* = 0.0001, 0.0002, 0.0005, 0.001, 0.002$ and 0.005 .

In the case of the salts of the higher valence types the conductance values at the highest dilutions for which data exist are

represented by a square-root law, but the values of the limiting slope, α^* , are much higher than that demanded by the theory. This is indicated in table 5 which, like tables 3 and 4, has been

TABLE 3
Conductance data for electrolytes of type 1-1. Solvent water

$$\alpha_{\text{theor.}}^* = 35.7 + 0.159\bar{\Lambda}_{\infty}^*$$

ELECTROLYTE	$\bar{\Lambda}_{\infty}^*$	$\alpha_{\text{exp.}}^*$	$\alpha_{\text{theor.}}^*$	$\alpha_{\text{exp.}}^* - \alpha_{\text{theor.}}^*$
LiCl.....	98.9	57.4	51.4	6.0
LiIO ₃	67.4	48.3	46.4	1.9
LiNO ₃	35.2	56.3	50.9	5.4
NaCl.....	108.9	54.7	53.0	1.7
NaIO ₃	77.4	51.4	48.0	3.4
NaNO ₃	105.3	58.3	52.5	5.8
KCl.....	129.9	59.9	56.4	3.5
KBr.....	132.0	62.2	56.7	5.5
KI.....	130.5	51.5	56.5	-5.0
KIO ₃	98.4	54.2	51.4	2.8
KClO ₃	119.5	58.2	54.7	3.5
KNO ₃	126.4	65.7	55.8	9.9
KCNS.....	121.0	54.1	55.0	-0.9
CsCl.....	133.1	53.8	56.9	-3.2
AgNO ₃	115.8	62.4	54.1	8.3
TiNO ₃	127.6	63.4	56.0	7.4

TABLE 4
Conductance data for electrolytes of type 1-2. Solvent water

$$\alpha_{\text{theor.}}^* = 53.55 + 1.084 \frac{q}{1 + \sqrt{q}} \bar{\Lambda}_{\infty}^*$$

ELECTROLYTE	$\bar{\Lambda}_{\infty}^*$	$\alpha_{\text{exp.}}^*$	$\alpha_{\text{theor.}}^*$	$\alpha_{\text{exp.}}^* - \alpha_{\text{theor.}}^*$
Ba(NO ₃) ₂	117.0	92.8	86.9	5.9
Sr(NO ₃) ₂	113.4	97.8	85.5	12.3
CaCl ₂	116.7	88.0	86.1	1.9
Ca(NO ₃) ₂	113.6	97.4	85.6	11.8
MgCl ₂	110.9	83.2	84.1	-0.9
K ₂ SO ₄	132.2	81.0	92.1	-11.1

adopted from the article of Onsager (12). The values of α^* were calculated from the conductance data of Kohlrausch at the concentrations $\gamma^* = 0.0001, 0.0002, 0.0005, 0.001$ and 0.002 . It

appears as if the experiments had not as yet been carried out at high enough dilutions to be able to apply the limiting law, since the extrapolation to $\gamma^* = 0$ gives a value for which $\bar{\Lambda}_\infty^*$ is always too large.

TABLE 5
Conductance data for electrolytes of type 2-2. Solvent water

$$\alpha_{\text{theor.}}^* = 71.4 + 0.636 \bar{\Lambda}_\infty^*$$

ELECTROLYTE	$\bar{\Lambda}_\infty^*$	$\alpha_{\text{exp.}}^*$	$\alpha_{\text{theor.}}^*$	$\alpha_{\text{exp.}}^* - \alpha_{\text{theor.}}^*$
MgSO ₄	114.7	242.7	144.4	98.3
CdSO ₄	115.8	270.7	145.1	125.6

TABLE 6
Conductance data for electrolytes of type 1-1. Solvent methyl alcohol

$$\alpha_{\text{theor.}}^* = 109 + 0.626 \bar{\Lambda}_\infty^*$$

ELECTROLYTE	$\bar{\Lambda}_\infty^*$	$\alpha_{\text{exp.}}^*$	$\alpha_{\text{theor.}}^*$	$\alpha_{\text{exp.}}^* - \alpha_{\text{theor.}}^*$
LiCl.....	90.9	158	166	-8
NaCl.....	97.0	163	170	-7
KCl.....	105.1	185	175	10
RbCl.....	108.7	199	177	12
CsCl.....	113.6	200	180	20
KF.....	94.0	167	168	-1
KBr.....	109.4	185	178	7
KI.....	114.9	184	181	3
NH ₄ Cl.....	111.0	187	179	8
HCl.....	193.5	260	231	29
LiNO ₃	100.3	177	172	5
NaNO ₃	106.5	204	177	27
KNO ₃	114.6	244	181	63
RbNO ₃	118.2	251	183	68
CsNO ₃	123.0	268	186	82
AgNO ₃	113.0	319	180	139
NaBr.....	101.5	170	173	-3
NaOCH ₃	98.4	157	171	-14
NaClO ₄	115.1	198	181	17

For the solvent methyl alcohol at 25°C. (Dielectric Constant 30) the coefficient becomes

$$\alpha^* = 1.07 w \bar{\Lambda}_\infty^* + 54.5 (z_a + z_c)$$

The data of Fraser and Hartley (8) have been used by Onsager for the verification of the limiting conductance expression. The range of concentration considered was $\gamma^* = 0.0001$ to 0.002 as in the case of the aqueous solutions. The comparison of the experimental results with the theoretical is given in table 6. Many of the differences at least must be considered as real deviations from the limiting law. It seems probable that in the region of concentration studied many of the electrolytes are associated to a certain degree, and that if the data were available for the region $\gamma^* = 0.00001$ to 0.0001 a better agreement with the theory might be expected.

Examining the work of Walden, Ulich and Busch in the solvent acetone it is found that the change of conductance in the dilute solutions may be represented by a square-root law. However, simple calculations carried out by the present authors indicate that the values for the constant α^* determined from the experimental data are much greater than that given by the theory, again indicating a certain degree of association of the ions.

The authors believe that satisfactory experimental verification of the theory in any solvent having a dielectric constant much below that of water will only be possible in solutions which are more dilute than any which have as yet been studied. The same thing is true in the case of aqueous solutions of salts of the higher valence types.

Thus the present position of the conductance theory may be compared to that of the activity theory which, although it has been amply verified in aqueous solutions, cannot as yet be said to have been proven satisfactorily in solvents of considerably lower dielectric constant. It is true that several attempts have been made in this direction using electromotive force measurements (14). More recently one of us (15) has published data which indicate that the activity theory is obeyed for salts of the type 1-1 and 1-2 in methyl alcohol in sufficiently dilute solution. The activity coefficients were determined by means of the effect of suitable solvent salts on the solubility of highly insoluble complex cobaltammine salts in that solvent. The solubility of the saturating salts in methyl alcohol is considerably less than it

is in water. Since the same salts and salts of similar solubility had previously been used to verify the theory in aqueous solution (16), it is probable that if the necessary measurements can be made on sufficiently dilute solutions a verification will be possible.

The experimental data in the various solvents which have been utilized above in the verification of the simple conductance theory are for the most part for solutions whose lowest concentration is not less than 0.0001 mol per liter, and whose highest concentration is not greater than 0.005 mol per liter. The figures seem to indicate that 0.0001 mol per liter is sufficient dilution only in the case of the conductance effect of salts of the simpler valence types in water. In the case of the activity theory the straight line relationship between the logarithm of the activity coefficient and the square root of the ionic strength, and with the correct slope, has been shown to hold in many cases up to concentrations of the order of magnitude of 0.01 mol per liter. The difficulties of verification of the simple conductance theory are therefore greater than in the case of the activity theory. One reason is, without doubt, that it is necessary to use a number of complicating assumptions in calculating the limiting slope in the case of the conductance theory. It may be suggested here that with improvements in the technic of conductance measurements at high dilutions, at least certain of the difficulties which the theory has met will be overcome.

III. THE DEPENDENCE OF THE ELECTRICAL CONDUCTANCE ON FREQUENCY

In the preceding section the theory which describes the conductance of dilute solutions of strong electrolytes for the usual type of conductance measurement has been reviewed. It will be recalled that for this measurement the Vreeland oscillator, the ordinary vacuum tube generator, the induction coil, or the Washburn generator are standard sources of the alternating current which are used to reduce electrolytic disturbances and polarization effects to a minimum. These instruments are styled in textbooks as sources of "high-frequency" current. In the discussion given for this type of conductance it was recognized

that the thickness of the ionic atmosphere was of primary importance.

The purpose of the present section is to show that as a necessary consequence of the existence of a finite time of relaxation, an electrical conductance which is dependent on the frequency must result. From the examples to be given it will be apparent that the frequencies of the sources mentioned in the paragraph above are not high enough to cause any appreciable effect on the conductance of the solution. In other words, to measure the predicted effect it will be necessary to resort to such sources as the Holborn sender or especially built vacuum tube generators which will operate to give waves of length of the order of magnitude 1 to 10 meters.

Consider an ion, surrounded by its ionic atmosphere, to be suddenly removed from the solution. The regular distribution of the ions in the neighborhood of this ion can no longer exist, because the central force field which is the cause of the regular distribution has been removed. The change of the distribution of the charges of the ionic atmosphere to a random distribution with respect to the point where the central ion was will take place gradually. The disappearance of this equilibrium position has been given both mathematically and in the form of a graph in the original articles (17). In the first article this process which is described above was treated only for the case of a symmetrical electrolyte whose ions possessed equal mobilities and neglecting the effect of their Brownian movements. The general case of an unsymmetrical electrolyte, taking into consideration the Brownian movements of the ions is considered in the second article. To summarize the results of these calculations, the statement may be made that the *time of relaxation* is a measure for the disappearance of the equilibrium condition. It has already been shown that it is of the order of magnitude $\frac{10^{-10}}{\gamma}$ seconds.

The reason why a dispersion or frequency dependence of the electrical conductance must exist may be explained in the following manner. If an ion is in motion due to the action of an external electrical field, then, as we have seen in Part II, there

will be a density of charge (of opposite sign) which is too small before and too large behind any ion upon which attention is fixed. Therefore, there will be a dissymmetry of the ionic atmosphere which becomes more and more important the greater the average velocity of the ion is. The result is the resisting force which has been called the electrical force of relaxation in Part II. This electrical force of relaxation appears in the calculation (as is shown by equation (28)) as a decrease in the mobility of the ion.

It must be emphasized that the calculation of the dissymmetry can give an approximation only for small ionic velocities. In the usual cases an approximation is sufficient but the case is different when one, as has been done by Wien (18) in his recent experiments, causes the existence of abnormally large ionic velocities by great field strengths. The order of magnitude of the ionic velocities in the Wien experiments was 1 meter per second contrasted to the usual velocities of the order of magnitude 0.01 mm. per second. It can be readily shown that ions which have these high velocities will travel many times the thicknesses of their ionic atmospheres in the time of relaxation. Under these conditions, then, the ionic atmosphere can hardly be built. Therefore, in very strong fields the force which has been termed the additional electrical force of relaxation is of little or no consequence, and the conductance will approach that value found at infinite dilution. This deviation from Ohm's law is exactly the effect discovered experimentally by Wien and explained in a more or less quantitative manner by Joos and Blumentritt (19). This effect has also been discussed in some detail from the standpoint of the interionic attraction theory by the authors (20). It has been introduced at this point merely to assist the reasoning which leads to the explanation of the dispersion effect.

To return to the point in question, it may be said that if the experiments of Wien can be explained in the manner which has been given, and the explanation is certainly beyond reasonable doubt the correct one, then the existence of an electrical conductance which is dependent on the frequency must be suspected. If it be assumed that an outer electrical field of oscillation fre-

quency ω acts on the ions in the solution, then apart from their Brownian movements the ions must acquire a back and forth, or periodic movement. For the ordinary frequencies it can be shown that the ionic atmosphere will have in each moment a dissymmetry of distribution of charges which corresponds to the momentary velocity of the ion. In other words, the decrease in the conductance of a solution due to the electrical force of relaxation will be independent of frequency until the extreme case where the frequency of the field is extraordinarily great compared to $\frac{1}{\theta}$ is reached. Under these conditions it may be shown (17), (20) that the dissymmetry of the ionic atmosphere cannot be built. If the frequency is made high enough, it should then be possible to almost completely destroy this electrical force of relaxation. Since this force is one which in the case of the frequencies ordinarily used for the measurement of conductance operates to resist the passage of an ion, it is evident that an increase in conductance will appear when such high frequencies are used that this force disappears. It is, therefore, predicted (17) that for sufficiently high frequencies an electrical conductance which is dependent on the frequency will result.

The results of the original calculations for the general case of an unsymmetrical electrolyte, taking into consideration the Brownian movement of the ions are given below. The molecular conductance, $\bar{\Lambda}$, as a function of the frequency may be written:

$$\bar{\Lambda} = \bar{\Lambda}_{\infty} - \bar{\Lambda}_{Iw} - \bar{\Lambda}_{II} \quad (33)$$

where $\bar{\Lambda}_{\infty}$ = molecular conductance at infinite dilution.

$$\bar{\Lambda}_{Iw} = \frac{|\epsilon_1 \epsilon_2|}{3 D k T} \kappa \bar{\Lambda}_{\infty} \bar{\kappa} (\omega \theta, q) \quad (33,a)$$

= electrical force of relaxation for frequency ω .

$$\bar{\Lambda}_{II} = \frac{n_1 \epsilon_1^2 + n_2 \epsilon_2^2}{6 \pi \eta} \cdot \frac{1000}{\gamma} \frac{1}{9 \times 10^{11}} \cdot \kappa \quad (28,b)$$

$$\bar{\kappa} = \frac{\sqrt{q}}{\left(1 - \frac{1}{q}\right)^2 + \omega^2 \theta^2} \left[\left(1 - \frac{1}{q}\right) \left(\bar{R} - \frac{1}{\sqrt{q}}\right) + \omega \theta \cdot \bar{Q} \right]$$

$$\bar{R} = \frac{1}{\sqrt{z}} \sqrt{\quad}$$

$$\bar{Q} = \frac{1}{\sqrt{z}} \sqrt{\quad}$$

$$z_1^2 z_2^2 \quad 15.34 \times 10^{-8}$$

$$z_1^2 \bar{L}_1 + z_2^2 \bar{L}_2 \quad k T q \kappa^2$$

κ^2 being given by equation 28,c

The dependence of the conductance on frequency appears in the term \bar{X} , which is in turn dependent on $\omega\theta$ and q . The values of θ in terms of the concentration for several electrolytes with the corresponding wave lengths in meters, have already been given in table 2. The frequency ω is controlled experimentally. It is evident from the equations (33) that in the case of ordinary frequencies the expression for the molecular conductance goes over to that given by equations (28). It is thereby assumed that the electrophoretic part of the conductance is independent of the frequency. The quantity, q , is given by equation (29).

Values of the quantity $\bar{\Lambda}_{I\omega}/\bar{\Lambda}_{I_0}$, also dependent on $\omega\theta$ and q , have been used to demonstrate the magnitude of the effect of frequency on conductance (17), (21). In these articles a detailed description of the effect of such factors as concentration of the solution, mobilities and valences of the ions, dielectric constant of the medium, and temperature has been given. It is not our purpose to review this material here, it will be sufficient to include a single graph (fig. 1) to show the dispersion effect quantitatively. In this figure, which illustrates the effect of a change in the valences of the ions, values of the quantity $\bar{\Lambda}_{I\omega}/\bar{\Lambda}_{I_0}$ are plotted against the wave lengths, for which a logarithmic scale has been used. Wave lengths for which the electrical force of relaxation has been reduced to one-half its usual value, i.e., when $\bar{\Lambda}_{I\omega}/\bar{\Lambda}_{I_0} = 0.5$, may be read directly from the graph for each of the salts for which curves are given.

In order to indicate the magnitude of the effect under discussion we shall consider a 0.001 molal solution of cadmium sul-

fate. The molecular conductance at infinite dilution and 18°C. is

$$\bar{\Lambda}_{\infty} = 92 + 136.6 = 228.6$$

The calculated decrease in conductance due to the electrophoretic effect is, according to equation (28).

$$\bar{\Lambda}_{II} = 12.8 = 5.6 \text{ per cent of } \bar{\Lambda}_{\infty}$$

The calculated decrease in conductance due to the electrical force of relaxation for the ordinary frequencies is, also according to equation (28)

$$\alpha_{I_0} \quad 13.0 = 5.7 \text{ per cent of } \bar{\Lambda}_{\infty}$$

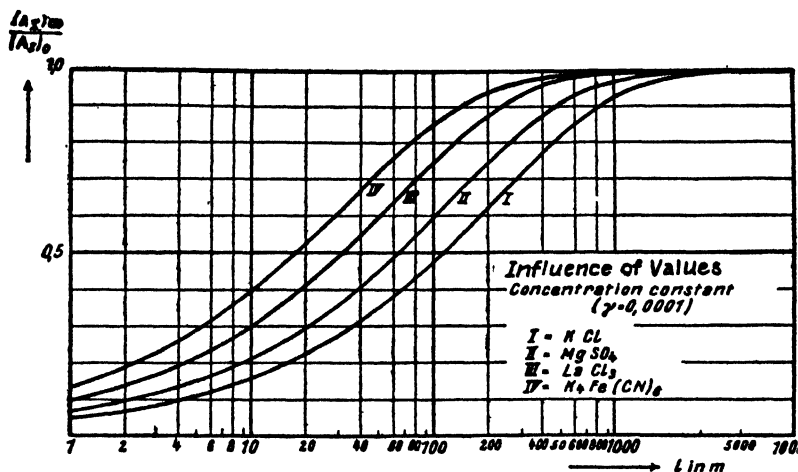


FIG. 1

At a wave length of 6.5 meters $\bar{\Lambda}_{Iw}/\bar{\Lambda}_{I_0} = 0.5$, therefore,

$$\bar{\Lambda}_{Iw} = 6.5 = 2.85 \text{ per cent of } \bar{\Lambda}_{\infty}$$

Therefore, if a source of current having a frequency corresponding to a wave length of 6.5 meters is used to measure the conductance of a 0.001 molal solution of CdSO₄, its molecular conductance should be approximately 3 per cent higher than that measured using a frequency corresponding to a wave length of 300 meters, for example.

The example of $\text{K}_4\text{Fe}(\text{CN})_6$ is similar. The molecular conductance at infinite dilution and 25°C . is

Further,

$$\bar{\Lambda}_{II} = 18.9 = 2.8 \text{ per cent of } \bar{\Lambda}_\infty$$

$$\bar{\Lambda}_{Io} = 13.7 = 2.0 \text{ per cent of } \bar{\Lambda}_\infty$$

The total lowering of the molecular conductance is 4.8 per cent. An increase of approximately one per cent in the molecular conductance should be observed using the wave length, $l = 16.3$ meters, i.e., where $\bar{\Lambda}_{Iw}/\bar{\Lambda}_{Io} = 0.5$. The curve for this salt is given in figure 1. The maximum dispersion effect, to be observed at extremely short wave lengths, would be of the order of magnitude of 2 per cent.

The predicted effect has been observed for the first time by Sack (22), working here in Debye's laboratory. This observation must, however, be considered to be one which is as yet but roughly qualitative in nature. A quantitative verification will of course consist in being able to show that a series of experimentally determined conductances for various short waves will give a curve which when properly plotted will coincide with the corresponding calculated curve. Such calculated curves are given in figure 1.

The effect in question is already finding application to chemical problems. For example, Nernst (23) has utilized it, in combination with the classical Arrhenius theory, to calculate a degree of dissociation for strong electrolytes in solution. Further, it now seems possible that the effect of the mutual association of the ions may be determined by a direct experiment. With the elimination of this factor a true degree of dissociation should be made accessible.

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KINETICS OF CHAIN REACTIONS

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The study of a considerable variety of homogeneous gaseous reactions has revealed that their kinetics can be interpreted on the basis of a theory advanced already in main outline by Arrhenius. According to this theory only the so-called activated molecules can enter into reaction. The number of these molecules is a function of temperature and of the gaseous concentrations and therefore the reaction velocity is also a function of these parameters. The number of activated molecules may sometimes change very rapidly with temperature (when the "activation energy" is very large) and concentration but this change remains always steady and continuous and so should the reaction velocity.

Still, a large number of reactions are known, the rate of which, although homogeneous, shows a peculiar discontinuous dependence on the outside parameters. To this type of reactions belong, for instance, the phenomena of explosions and inflammations, in which the rate changes from, occasionally, immeasurably small values to exceedingly large ones as the result of only negligibly small changes in the parameters—the temperature and the pressure of the reaction body.

An opinion exists that such behavior is not in disagreement with the activation theory of Arrhenius. Namely, the heat evolved in the rather slow initial stages of a reaction must heat up somewhat the reaction mixture. This results in an acceleration of the reaction velocity owing to its high temperature coefficient. If the conditions are such that, at all times, the heat losses by the gas mixture to the outside are less than the heat supplied by the

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reaction, the warming up and therefore the reaction velocity will be auto-accelerated ad infinitum (or until the reaction is over) and this phenomenon constitutes an explosion. As the writer has previously shown (1), such interpretation of the explosion mechanism leads to the conclusion that, for each composition and total pressure of the reacting mixture, there exists a certain critical temperature below which an explosion is impossible and above which an explosion will occur. The critical temperature is dependent on the pressure of the explosive mixture and for each critical temperature there exists a critical pressure above which an explosion occurs and below which only a slow, sometimes a very slow, reaction takes place. The relation between the critical pressure and the critical temperature is expressed by the equation

$$\log p = \frac{A}{T} + B \quad (1)$$

where the constant A is dependent on the energy of activation only, whereas the constant B depends on the composition of the reaction mixture and on the conditions of the heat conductance from the reacting gases. Testing this relation experimentally Sagulin (2), has found it confirmed in a considerable number of explosive gaseous mixtures.

Nevertheless there exists very strong evidence indicating that such a theory of "thermal" explosions is incorrect in the majority of cases and that therefore an interpretation of the explosion phenomena by means of the classical concepts of chemical kinetics (the theory of Arrhenius) is, generally speaking, impossible.

First of all, there are a number of explosive reactions in which the temperature of the flame is quite low, sometimes hardly exceeding room temperature. Of this type are, for instance, the burning of ether and of carbon bisulfide in oxygen, but, particularly striking is this type of reaction exhibited in the oxidations of the vapors of phosphorus and of sulfur at low pressures.

Furthermore, there are a number of explosive reactions in which the critical pressure is independent of the temperature. Of this type are oxidations of phosphorus and of carbon monoxide. From the point of view of the theory of thermal explosions

indicated above, such behavior is possible only when the constant A (equation 1) is equal to zero and this means that the energy of activation is also equal to zero. But if $E = 0$, these reactions should be extremely rapid even when there is no inflammation. Instead, if phosphorus vapor is mixed with such amounts of oxygen that no inflammation occurs, the oxidation velocity, as has been shown by the writer (3), is extremely slow, no measurable reaction occurring for many hours. Similarly, a carbon monoxide-oxygen mixture, explosive at temperatures above a certain critical temperature, practically does not react at all if the temperature is maintained at only a few degrees below the critical value.

All such observations disagree with the assumption that the energy of activation of these reactions is equal to zero. The theory of thermal reactions thus is incapable of accounting for some of the experimental evidence. But it is not only the phenomenon of incandescence which indicates the insufficiency of the classical concepts of chemical kinetics. It is well known that frequently immeasurably small amounts of foreign substances influence radically the rate of chemical reactions. Perhaps the most striking effect of this type is the action of water vapor, discovered by Dixon and by Baker. Thus, for instance, sufficiently dried phosphorus and oxygen do not react at all; the photochemical formation of hydrogen chloride in visible light is stopped completely according to Coehn when the partial pressure of water vapor is less than 10^{-5} mm., but goes with normal velocity when this pressure exceeds 10^{-4} mm.

Polanyi (4) has shown that the dark formation of hydrogen chloride goes very rapidly if hydrogen contains traces of sodium vapor. Riabinin and the writer (5) succeeded in demonstrating that sulfur vapor in oxygen does not ignite at all at temperatures from 50 to 100°. However, a presence of infinitesimal traces of ozone in oxygen is sufficient to cause rapid combustion. Thus, the reaction either does not go at all or proceeds with a very high velocity depending only on whether there are traces of ozone present in the reaction vessel. Hinshelwood and Simpson (6) and earlier Dixon have found that small amounts of nitric oxide

decrease by 200° the explosion temperature of the hydrogen-oxygen mixture. A similar observation has been made by Sagulin and the writer (7) in the case of carbon monoxide-oxygen mixtures where the explosion temperature is decreased by 50° even when nitric oxide, being first admitted into an empty reaction vessel, is pumped out by a high vacuum pump before the reaction mixture is introduced. Under these circumstances the partial pressure of NO should not exceed 10^{-5} mm. Not less striking is the effect of negative catalysts or inhibitors. As has been shown in detail by Bäckström (8) the homogeneous rate of oxidation of aldehydes is reduced manyfold on addition of 0.01 per cent and less of certain inhibitors. Oxygen exercises a similar action on the photochemical formation of hydrogen chloride according to observations of Bodenstein. Different authors have demonstrated that addition of vapors of organometallic compounds increases the explosion temperature of hydrocarbons, thus inhibits the explosion.

All these and many other facts relating to homogeneous catalysis can hardly be reconciled with the classical theory of chemical kinetics.

A GENERAL THEORY OF CHAIN REACTIONS

Already at the first glance one weak point in the classical theory of chemical reactions becomes quite obvious. According to this theory, activated molecules are formed as the result of collisions of molecules whose relative kinetic energy exceeds the energy of activation E . Let us call n the number of activated molecules thus formed per unit time. Assuming that most of these activated molecules react before they are somehow de-activated, the rate of reaction, according to the theory of Arrhenius, is equal to n . The number n is calculated usually thus. The total number of molecular collisions per unit time is Z ; the activation occurs only when the relative energy of colliding molecules is larger than E ; the probability of this is $e^{-E/RT}$. Thus, according to the classical theory the number of reacting molecules is given by the equation

$$w = n = Z e^{-E/RT} \quad (2)$$

Such conclusion however is incorrect as has been pointed out already by Christiansen and Kramers. Indeed, each elementary reaction act is accompanied by an accumulation of energy equal to $E + Q$, where Q is the heat of reaction. This energy is transformed ultimately into heat energy, i.e., is distributed as kinetic and potential energy among all molecules of the gas. In the time immediately following the reaction process, on the other hand, all this energy is distributed as potential and kinetic energy among only those few molecules which are produced in the elementary process of reaction.

Let us assume that each of the molecules resulting in the reaction carries a part φ of the total energy $E + Q$. An activation will then occur on collision of some other molecules with the reaction product when the available energy of this molecule exceeds the magnitude $E - \varphi$. The probability of this process is $e^{-\frac{(E - \varphi)}{RT}}$. Thus, each primary reaction can lead to the formation of secondary reaction processes, the probability of such action being $\alpha = \alpha_0 e^{-\frac{(E - \varphi)}{RT}}$. It follows that the number of reacting molecules is expressed not by equation (2) but by:

$$w = n + \alpha w \quad (3)$$

which takes into account this secondary activation. Equation (3) leads to a general expression for the rate of reaction:

$$w = \frac{n}{1 - \alpha} \quad (3a)$$

When the magnitude α is equal to unity, each primary reaction process causes an infinite sequence of secondary reactions—an infinite reaction chain. And since the primary links of these chains (due to thermal activation) are produced to the number n per unit time, the total rate must be obviously infinite. This result is obtained also from equation (3a) when α is equal to unity. When α is less than unity the number of secondary links

produced by one primary reaction is finite and is equal to $\nu = \frac{1}{1 - \alpha}$. The quantity ν can be interpreted as the length of chain.

$$1 - \alpha - \beta \quad (4)$$

where by β is denoted the probability that the chain is stopped at any given link. It may happen also that α is larger than unity. This can occur for instance when the total energy $E + Q$ is larger than twice the activation energy E . Under these circumstances each primarily activated molecule may lead to the formation of two new activated molecules. When $\alpha > 1$, equation (3a) has no positive solution. A closer consideration of this case (1) has shown that, however small is n , the reaction velocity, once started, will increase auto-acceleratingly to infinity. The rate of increase is the more rapid, the larger is $\alpha - 1$. The chains are here not only infinitely long, but, besides, they branch out, causing new chains to be started independently of the primary activation.

Summarizing, the three possibilities: $\alpha < 1$; $\alpha = 1$; $\alpha > 1$; characterize the following processes: (1) $\alpha < 1$; the primary links in the chains are started by the primary activation. The length of each chain is finite. (2) $\alpha = 1$; the primary links on the chains are started by the primary activation. The chains are infinitely long. (3) $\alpha > 1$; the chains are infinite and are started not only by the primary but also by the secondary activation. They branch out and one primary activation starts not one but infinitely many infinitely long chains. This can be illustrated by figure 1.

The question may arise, in how far the new chemical kinetics here indicated satisfy the laws of thermodynamics. Assuming the reaction to be $A \rightleftharpoons B$ and the reaction velocities of both processes to be w_1 ($A \rightarrow B$) and w_2 ($B \rightarrow A$); instead of equation (3a), the equations (5) are obtained:

$$\begin{aligned} w_1 &= n_1 + \alpha_{11}w_1 + \alpha_{21}w_2 \\ w_2 &= n_2 + \alpha_{22}w_2 + \alpha_{12}w_1 \end{aligned} \quad (5)$$

Here n_1 and n_2 are the numbers of primarily activated and reacting molecules in the direct and in the reverse reaction. The coefficients a_{11} ; a_{22} ; a_{21} ; and a_{12} are defined in the following manner: a_{11} is the probability that a given primary process of the direct reaction results in the formation of a secondary process of the direct reaction; a_{22} is the same magnitude for the reverse reaction; a_{21} is the probability that a given elementary process of the reverse reaction leads to the formation of a reaction process of the direct reaction; a_{12} is the probability that a process of the direct reaction results in the formation of a process of the reverse reaction.

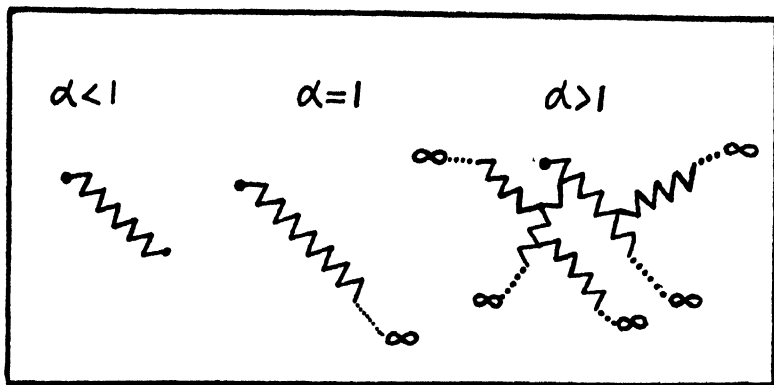


FIG. 1. THE REACTION CHAINS

Classical kinetics give $w_1 = n_1 = Z_1 e^{-E_1/RT}$ and $w_2 = n_2 = Z_2 e^{-E_2/RT}$ where E_1 and E_2 are the respective activation energies of the direct and of the reverse reaction.

Thermodynamics require that in the state of equilibrium the ratio of the velocities $\frac{w_2}{w_1}$ should be proportional, at least in the first approximation, to $e^{-Q/RT}$, where Q is the heat change accompanying the direct reaction $A \rightarrow B$. It follows therefore that

$$K = \frac{w_2}{w_1} = \frac{Z_2}{Z_1} e^{-\frac{E_2 - E_1}{RT}} = C e^{-Q/RT}; E_2 - E_1 \quad (6)$$

Thus, to satisfy thermodynamics, it is necessary only to assume (as has been pointed out already by Arrhenius) that the difference in the energies of activation is equal to the heat of reaction. But, as will now be shown, the same condition is sufficient to reconcile also the new equations (5) with thermodynamics.

The energy produced in each process of the direct reaction is equal to $E_1 + Q$. On the average each of the molecules of the reaction products carries a part φ of this energy. It follows that

$$\alpha_{11} = C_1 e^{-\frac{E_1 - \varphi}{RT}}$$

and

$$C_2 e^{-\frac{E_2 - \varphi}{RT}} \quad (7)$$

α_{11} indicating the probability that one of the reaction products collides with (and activates) a molecule A having an available thermal energy in excess of $E_1 - \varphi$ and α_{12} indicating the probability that the same reaction product collides with a molecule B having an energy in excess of $E_2 - \varphi$. When it is remembered that n_1 is proportional to the probability that a molecule having an energy in excess of E_1 collides with a molecule A and that n_2 is proportional to the probability that a molecule with energy E_2 collides with a molecule B, it will become evident that:

$$\frac{n_1}{n_2} = \frac{Z_1 e^{-E_1/RT}}{Z_2 e^{-E_2/RT}} = \frac{C_1 e^{-\frac{E_1 - \varphi}{RT}}}{C_2 e^{-\frac{E_2 - \varphi}{RT}}} = \frac{\alpha_{11}}{\alpha_{12}} \quad (a)$$

Similarly it follows that:

$$\frac{\alpha_{22}}{\alpha_{21}} = \frac{n_2}{n_1} \quad (b)$$

and, furthermore, the additional equation (c) can easily be derived:

$$\alpha_{11} \alpha_{22} = \alpha_{21} \alpha_{12} \quad (c)$$

Solving the system of equations (5) one obtains:

$$w_1 = \frac{n_1 (1 - \alpha_{22}) + \alpha_{21} n_2}{(1 - \alpha_{11}) (1 - \alpha_{22}) - \alpha_{12} \alpha_{21}}$$

$$w_2 = \frac{n_2 (1 - \alpha_{11}) + \alpha_{12} n_1}{(1 - \alpha_{11}) (1 - \alpha_{22}) - \alpha_{12} \alpha_{21}}$$

Making use of the equations (a), (b), (c) the following expressions are obtained:

$$w_1 = \frac{n_1}{1 - \alpha_{22} - \alpha_{11}}$$

$$w_2 = \frac{n_2}{1 - \alpha_{22} - \alpha_{11}}$$
(8)

Whence: $K = \frac{w_2}{w_1} = \frac{n_2}{n_1} = C e^{-Q/RT}$ in accordance with the law of equilibria. Van't Hoff, deducing from the thermodynamic equation (6), concluded that the rates w_1 and w_2 as functions of temperature must be represented by the expressions:

$$w_2 = C_2 e^{-E_2/RT} \quad \text{and} \quad w_1 = C_1 e^{-E_1/RT}; \quad E_2 - E_1 = Q;$$

but, assuming more generally:

$$w_2 = \frac{C_2 e^{-E_2/RT}}{\psi(T)} \quad \text{and} \quad w_1 = \frac{C_1 e^{-E_1/RT}}{\psi(T)} \quad (9)$$

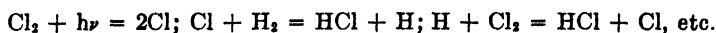
one still obtains expressions not in disagreement with the laws of equilibria, however fast may $\psi(T)$ change with T . Such more general type of temperature function for the rate of chemical reaction is the type which results from the application of the concepts of the chain theory. Consequently the Arrhenius-Van't Hoff equation:

$$\log w = -\frac{A}{T} + B$$

represents only a limiting case and can be approximately correct for those reactions only in which α is very close to zero or when it is independent of temperature.

THE FINITE CHAINS

The concept of reaction chains has been established as the result of a series of photochemical investigations. Thus, in the case of hydrogen chloride formation about 10^5 molecules of HCl are formed for one light energy quantum absorbed by chlorine. The length of chains is here therefore: $\nu = 10^5$, the probability that a chain is stopped at a given link $\beta = \frac{1}{\alpha} = 10^{-5}$ and the quantity $\alpha = 1 - \beta = 0.99999$. In all probability the chain is propagated in a way suggested by Nernst:



The secondary activation in this reaction consists in that, through the reaction of a chlorine atom with one hydrogen atom, the other atom of the hydrogen molecule is made free and becomes an active reaction center for the consecutive chain links. The above scheme corresponds, of course, to $\alpha = 1$, thus to infinite chains. The reason why the chains are finite in reality has been explained by Bodenstein and consists in a breaking off of the chains by oxygen molecules. According to Göhring (9) such action is due to the free atoms of chlorine and of hydrogen entering into reaction with oxygen and thus becoming incapable of continuing the chain. If one assumes that each collision of Cl or H with O_2 leads to reaction, the probability of stopping the chains will be expressed by

$$\beta = \frac{[\text{O}_2]}{[\text{Cl}_2]} + \frac{[\text{O}_2]}{[\text{H}_2]} \quad (10)$$

In a more general case this probability will be

$$\beta = k_1 \frac{[\text{O}_2]}{[\text{Cl}_2]} + k_2 \frac{[\text{O}_2]}{[\text{H}_2]}$$

and correspondingly the expression for the rate of reaction will be:

$$w = \frac{n}{\beta} = n \nu = \frac{n [\text{H}_2] [\text{Cl}_2]}{(k_1 [\text{H}_2] + k_2 [\text{Cl}_2]) [\text{O}_2]}$$

Considering that n — the number of primarily started chains — is proportional to the product of light intensity and concentration of chlorine (a case of weak absorption of light), the equation for the rate of reaction takes the form:

$$v = \frac{I_0 [\text{Cl}_2]^2 [\text{H}_2]}{(k_1 [\text{H}_2] + k_2 [\text{Cl}_2]) [\text{O}_2]}$$

which is in complete accord with experimental data. One can estimate the inhibiting action of oxygen assuming $k_1 = k_2 = 1$. Since in this case:

$$\nu = \frac{1}{\beta} = \frac{1}{\frac{[\text{O}_2]}{[\text{H}_2]} + \frac{[\text{O}_2]}{[\text{Cl}_2]}}$$

the chains will be about 1000 molecules long if the ratios $[\text{O}_2]:[\text{H}_2]$ and $[\text{O}_2]:[\text{Cl}_2]$ are of the order of magnitude of 10^{-3} ; when these ratios are about 10^{-5} , the chains are 10^5 molecules long. Thus, a change in oxygen concentration from 0.1 to 0.001 per cent changes the chain length a hundred-fold. This shows how the presence of very small amounts of impurities can change the rate of chain reactions and indicates once more the nature of negative catalysis or inhibition which has been treated decisively already by Christiansen (10). A particularly convincing experimental confirmation of this theory of inhibition has been obtained by Bäckström (8), (11) in his work on oxidation of aldehydes and of sodium sulfite solutions.

Of a very similar nature is the inhibitive action of the solid walls of the containing vessel, first described by the author (3) for the oxidation of phosphorus vapor, observed also by Hinshelwood and Simpson (6) and by Pease (12) for the thermal reaction of oxygen and hydrogen, by Pease (12) for the thermal oxidation of some hydrocarbons and recently observed by Triffonoff of this laboratory (7) in the case of photochemical HCl formation at low pressures. Such action of the walls is due undoubtedly to adsorption and de-activation on the walls of activated molecules (atoms of chlorine and hydrogen in the hydrogen chloride reaction), an effect which is similar to the action of oxygen in the hydrogen chloride reaction for instance.

Assuming, as a first approximation, that the diameters of all molecules are equal and using the Einstein-Smoluchowski diffusion expression, the writer could show (7), that in the case that the chains are not broken off homogeneously, i.e., in the gas mixture itself, the length of chains ν_0 , as determined by the inhibitive action of the walls, is given by:

$$\nu_0 = \frac{6 \pi x^2}{4 \lambda_0} [\text{H}_2] [\text{Cl}_2] \quad (11)$$

Here x is the distance from the origin of the chain to the wall and λ_0 the mean free path at unit total pressure. Calculating the magnitude of ν_0 at atmospheric pressure and for ordinary dimensions of the reaction vessel, one obtains values of the order of $\nu_0 = 10^9$. This figure, being considerably in excess of the experimentally determined length of chains in the HCl reaction, indicates that at such pressures the chains are broken off almost exclusively by action of oxygen in the gas mixture itself and the action of the walls is quite unimportant. However, when the pressure is decreasing, the chains will be more and more frequently stopped on the walls since ν_0 decreases as the square of the pressure, whereas the inhibition in the gas space remains constant, provided the relative concentration of oxygen is constant.

At sufficiently low pressures the length of the chains is fully determined by (11) and since the average value of x is proportional to the linear dimensions of the vessel (diameter in case of cylindrical vessels), a proportionality of the reaction velocity to the square of the dimensions of the vessel must be expected. This last inference from the theory has been fully confirmed by Triffonoff (7). Hinshelwood and Simpson (6) succeeded in showing that at temperatures near the explosion point, where the homogeneous rate predominates, the rate of water formation is much faster in an empty vessel than in a vessel filled with pieces of broken porcelain. Furthermore, according to these writers, additions of helium, argon or nitrogen accelerate the reaction velocity. This observation is also fully in accord with the theory of inhibition by the walls: neutral gas, by decreasing the mean

free path, decreases the diffusion to the walls and thereby increases ν_0 — the length of chains — and thus the total rate. The writer has compared the influence of inert gases found experimentally in the work of Hinshelwood and Simpson with the magnitude of the influence to be expected theoretically and has arrived at very good agreement.²

The action of homogeneous catalysts in chain reactions is exemplified particularly clearly in the experiments of Polanyi, mentioned previously, in which it was shown that chlorine and hydrogen react in the dark at low temperatures if hydrogen is first passed over molten sodium and carries with it traces of sodium vapor. Polanyi has given a complete interpretation of this effect by employing the chain theory. He has shown earlier that the reaction of chlorine with sodium vapor goes according to the scheme $\text{Cl}_2 + \text{Na} = \text{NaCl} + \text{Cl}$. Thus, a free chlorine atom is formed in each elementary process and this then starts, in the hydrogen-chlorine mixture, the usual Nernst-chain, the result being that for each reacted sodium atom hundreds and even thousands of HCl molecules are formed.

The function of a positive catalyst is thus to create artificially the initial links of the chains, when these cannot be formed by the thermal activation energy alone.

It is at least probable that the catalytic action of water vapor is similar in nature. Water molecules, either owing to their large electric moment or to some other as yet unidentified property, must be able to facilitate the formation of the initial chain links—the reaction centers—, the thermal energy alone being unable under the circumstances to achieve this result.

These suggestions do not exclude the possibility that the action of some of the known catalysts may be due to a selective destruction of inhibitors, which prevent otherwise the normal course of a reaction.

² Using, as before, the Einstein-Smoluchowski expression and assuming all molecular diameters to be equal, the equation (11) can be generalized to:

$$\nu_0 = \frac{6\pi \times 10^8}{4\lambda_0^2} [\text{H}_2] [\text{Cl}_2] \left(1 + \frac{[\text{A}]}{[\text{H}_2] + [\text{Cl}_2]} \right) \quad (12)$$

Here [A] denotes the partial pressure of the inert gas. The expression can be used, suitably modified, for the present reaction also.

THE INFINITE CHAINS

The velocity of a reaction $w = \frac{n}{1 - \alpha}$ becomes infinite when α exceeds unity. The magnitude of α which is a function of temperature and of the concentrations of the reacting gases, changes

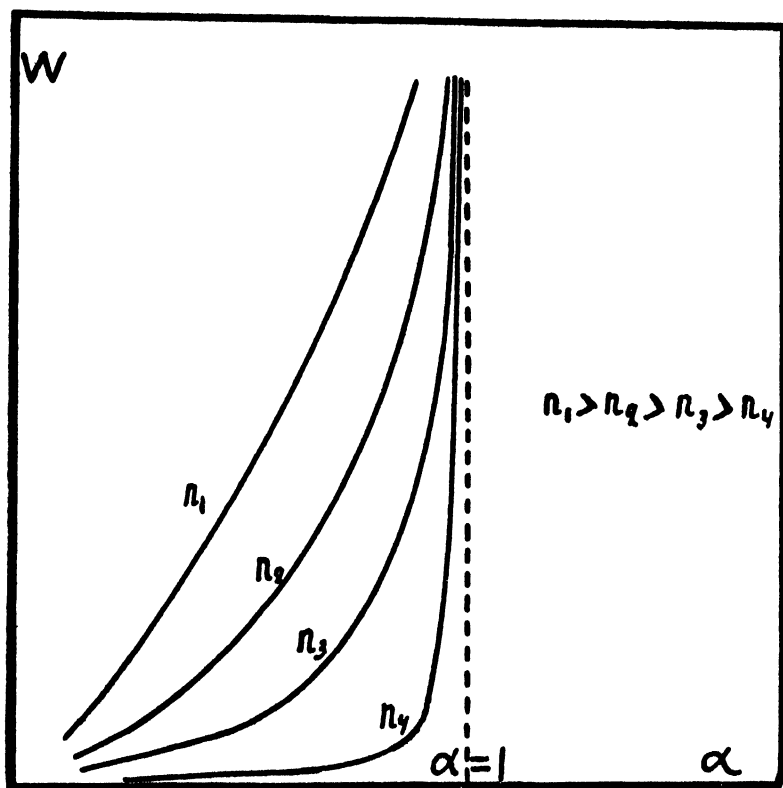


FIG. 2. REACTION VELOCITY AS A FUNCTION OF α AND n

with the change of these parameters and, being less than unity under some conditions, may exceed unity when the conditions are suitably altered. Plotting the rate of reaction as a function of α one obtains curves of the type presented in figure 2. They all yield $w = \infty$ when $\alpha = 1$. The smaller is n , the more rapid is the change from the condition in which the rate is practically

zero to the condition of infinite velocity. Thus an idea can be formed of the critical region in which a reaction goes over into inflammation or explosion, since this latter means a reaction of extremely high velocity. One can say that all chemical reactions in which α exceeds unity are inflammations or explosions and that the condition $\alpha = 1$ determines the region where a normal reaction becomes auto-accelerating or explosive. It becomes important to investigate how α can exceed unity in concrete cases. Let us consider, for example, the hydrogen-chlorine reaction again, which, as it is well known, can become explosive under suitable conditions.

The mechanism of this reaction has been discussed before:



At first glance the impression may be gained that here α can be either less or equal to unity but never more. That this is not so, the following consideration indicates. Reaction (3) is accompanied by an energy evolution of 45,000 cal. per mol. This energy must be distributed between the two resulting particles HCl and Cl. Let us assume that one of these carries the larger portion of this energy equal to φ . If this activated molecule collides with a chlorine molecule having itself 56,000- φ cal. energy, two new chlorine atoms will be formed, and thus two new chains originated. The probability of this process is

$$C e^{-56000-\varphi/RT} = C e^{-U/RT}$$

The coefficient C in this expression is of the order of unity and may be a function of the partial pressures of hydrogen and of chlorine.³

³ For instance, if it is assumed that the energy φ is lost on every collision with molecules of hydrogen or with molecules of chlorine having energy less than U , the quantity C is expressed by:

$$C = 2 \frac{[\text{Cl}_2]}{[\text{H}_2] + [\text{Cl}_2]}$$

If this energy is not lost on collisions with hydrogen but only on collisions with chlorine having energy less than U , the coefficient is:

Not considering the possibility of this secondary formation of chlorine atoms we would have the expression $\alpha_0 = 1 - \beta_0$, where β_0 stands for the probability of a given chain being broken. Taking the secondary atom formation with the probability $e^{-U/RT}$ into account, an expression for α is obtained which can be written thus:

$$\alpha = 1 - \beta_0 + C e^{-U/RT} \quad (13)^4$$

Expression (13) is less than unity at low temperatures but must become larger than unity at some temperature T_k . From this we may conclude that T_k is the critical temperature of explosion for a given hydrogen-chlorine mixture. Thus the condition for occurrence of explosion can be written:

$$\beta_0 = C e^{-U/RT} \quad (14)$$

Considering that the coefficient C for a given composition of the gas is independent of the total pressure, whereas the magnitude β_0 is probably proportional to some negative power of it,⁵ the

$$C = 2$$

If this energy, even on collisions with chlorine, is lost only on every n th collision, the coefficient is:

$$C = 2n$$

It should be pointed out furthermore that for a given composition of the gas the coefficient C is independent of the total pressure, even if the first of the above assumptions is the correct one.

⁴ To avoid misunderstanding it is appropriate to point out why earlier in this article we defined the probability of a chain being broken as equal to $\beta = 1 - \alpha$, whereas now the expression (13) is derived. This is due to the circumstance that β_0 of equation (13), is, according to its definition, the probability of a chain being broken without reference to a possible branching off. The true magnitude of β —the probability of a complete disappearance of a chain with all its branching, is:

$$\beta = \beta_0 - C e^{-U/RT}$$

⁵ When all the chains are broken off on the walls β_0 is: (cf.) equation (11))

$$\beta_0 = \frac{1}{\nu_0} = \frac{K_1}{[H_2] [Cl_2]} = K p^{-2}$$

On the other hand when all the chains are ended in the gas phase by oxygen alone, β_0 is (compt. equation (10)):

$$\beta_0 = [O_2] \left(\frac{1}{[H_2]} + \frac{1}{[Cl_2]} \right) = K p^0$$

equation (14) can be written:

$$K p^{-n} = C e^{-U/RT}$$

or:

$$\log p = \frac{U}{n RT} + B = \frac{A}{T} + B$$

This is a relation which was found experimentally by Sagulin (2) to hold for a large variety of explosive gaseous mixtures. As was pointed out in the beginning of this article, this expression was derived theoretically for the "thermal" explosions, that is for explosions occurring according to the classical views on chemical kinetics. The above shows in addition that a chain explosion also may yield the same relation between critical pressure and temperature. It must be pointed out in addition that the chain theory does not exclude that a "thermal" explosion may not precede the chain explosion, since autoacceleration caused by superheating may occur when α is still less than unity. Accordingly other characteristics of the explosions must usually be adduced in order to decide whether an explosion is of the chain- or of the thermal-type. The explosions of carbon disulfide-oxygen mixtures, for instance, which give a linear relationship between $\log p$ and $\frac{1}{T}$ with an angle of inclination indicating large

A , are undoubtedly chain explosions since the flame is quite cold and is very sensitive to the presence of traces of impurities. There are sufficient grounds for assuming also that the explosions of saturated hydrocarbons with oxygen are similarly chain explosions. In agreement with this, for instance, is their known sensitivity to various "antiknocks" present even in minute quantities. The nature of the explosions of $H_2 + Cl_2$ or of Cl_2O , on the other hand, is somewhat uncertain at present, although, in the opinion of the writer, here also we are hardly dealing with straight thermal explosions.

The chain explosion type is most clearly represented in the

reactions of phosphorus and sulfur vapors and of carbon monoxide with oxygen and these will now be considered here in some detail, being the basis of the explosion theory here developed.

INFLAMMATIONS OF PHOSPHORUS, SULFUR, AND CARBON MONOXIDE

It has been known for a long time that phosphorus vapor undergoes rapid combustion only when the oxygen pressure is maintained within certain limits. Jorissen (13), in particular, has considered the limiting pressures as the critical explosion limits and has investigated more in detail the upper critical oxygen pressure. The question of the lower limit of the oxygen pressure was, however, scarcely investigated until the writer and his collaborators became interested in this phenomenon. The researches resulted in discovery and investigation of several somewhat unusual characteristics of the—as it was named—residual pressure. When oxygen is slowly admitted through a capillary into an evacuated vessel in which some white phosphorus is present, the pressure increase during an initial time interval manifests the absence of any reaction. When the oxygen pressure reaches a certain value p_r , a sudden visible inflammation occurs and thereafter phosphorus vapor continues to burn. During this period no pressure increase can be observed which indicates that all newly admitted oxygen is immediately consumed in the reaction. The walls of the vessel become gradually covered by a non-transparent layer consisting probably of P_2O_5 and of red phosphorus. When the further flow of oxygen is interrupted the luminous reaction is instantaneously extinguished, whereby the pressure remains equal to the critical value p_r . This last feature of the process was the one which suggested the name residual-pressure for the critical pressure p_r . That the remaining gas is oxygen is evident for instance from the observation that this gas is not condensed in liquid air. The residual oxygen may be in contact with phosphorus for many hours without any reaction taking place. This has been established not only by the constancy of the residual pressure but also by the observation that when the flow of oxygen into the vessel is resumed, inflammation takes place instantaneously, instead of

occurring, as was described before, only after a certain time. The existence of the residual pressure was demonstrated furthermore in the following way. A mixture of phosphorus vapor and oxygen at a pressure less than p_r is gradually compressed; only when the pressure reaches a perfectly definite value a sudden inflammation occurs.

The residual pressure of oxygen is a function of the size of the vessel and of the pressure of the phosphorus vapor. With saturated phosphorus vapor at room temperature and in vessels of a few cm. in diameter it is of the order of 10^{-2} mm. mercury. At the time of inflammation, as well as during the following combustion, the temperature of the gas mixture is raised only very little judging from the absence of any pressure increase.

Studying the laws governing the residual pressure, without however very great precision being achieved, the following results were obtained by the writer:

1. p_r is independent of the temperature of the vessel.
 2. p_r is inversely proportional to some power n of the pressure p_A of phosphorus vapor; n is between 0.5 and 1.
 3. p_r is inversely proportional to some power r of the diameter of the vessel; r is between 1.5 and 2.
 4. p_r is decreased on diluting phosphorus vapor by argon.*
- The relation between p_r and the pressure of argon p_A follows very closely the following expression:

$$p_r \left(1 + \frac{p_A}{p_r + p_A} \right) = \text{const.}$$

All these regularities can be united in a single equation (15):

$$p_r p_A^m d^n \left(1 + \frac{p_A}{p_r + p_A} \right) = \text{const.} \quad (15)$$

On the whole it is obvious that phosphorus vapor and oxygen will either not react at all or react with an extremely high velocity,

* This last phenomenon is very distinct. One can take, for instance, a mixture of phosphorus vapor and oxygen below the p_r pressure and begin admitting argon into the vessel. At some definite pressure of this latter, inflammation occurs.

and the transition between these two states occurs within an unusually narrow interval in the values of the external parameters. Furthermore, that parameter which plays the main rôle in most of the explosions—the temperature—has no effect on this reaction.

In addition to the lower critical pressure of oxygen there exists also an upper critical pressure above which similarly no inflammation occurs. The phenomenon of this upper critical pressure has been described by several authors, who state that the value of the critical pressure is extremely sensitive to the presence of minute quantities of various substances. Quite recently a study of this phenomenon and an extension of the experiments on the lower critical pressure has been undertaken also in this laboratory (7).

The procedure was to admit oxygen into a vessel containing phosphorus and cooled by liquid air, then warm up the vessel to some definite temperature. If no inflammation occurred, oxygen was gradually pumped out through a capillary. At some pressure the inflammation occurred and went over usually into a violent burning of the phosphorus, followed frequently by destruction of the apparatus. The upper critical pressure of oxygen investigated from a few mm mercury to a pressure of nearly one atmosphere was found to be independent of temperature and to be directly proportional to the pressure of phosphorus vapor. The value of p_{\max} , which it attains with phosphorus vapor saturated at room temperature, is near to 600 mm. Thus, the relation between critical phosphorus and the upper oxygen pressure is:

$$\frac{p_{F_4}}{p_{\max}} = \text{const.} \quad (15a)$$

which means that when the percentage concentration of phosphorus decreases below a certain value, no inflammation can occur. A relation of this type is known to hold for almost all explosive mixtures, and it has frequently been observed that the presence of foreign substances can influence the value of the critical percentage concentration.

Extending earlier experiments of the writer on the residual pressure of oxygen to lower vapor pressures of phosphorus, Kowalsky was able to show that the equations of the upper and of the lower critical pressure of oxygen are nothing but the two limiting cases of the same general relation determining the explosion conditions of the phosphorus-oxygen mixtures. A

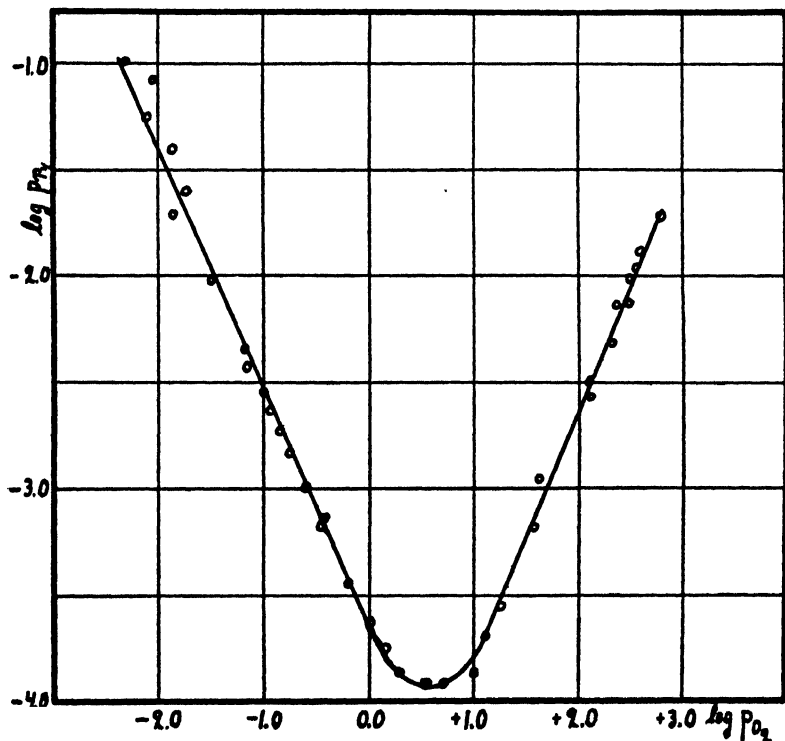


FIG. 3. INFLAMMATION LIMITS FOR $P_4 + O_2$ MIXTURES

transition region was found in which both curves flow smoothly together. These and our earlier experiments are represented on figure 3 in which the abscissae are the logarithms of the oxygen and ordinatae the logarithms of the phosphorus pressures (both in mm. mercury) and the region above the curve ABC is the explosion range.

When a comparison is made between the usual diagram of the

explosion pressure as a function of composition (fig. 4) and the laws governing the combustion of phosphorus, a very great similarity is found.⁷ The only difference is that the total critical explosion pressure in the middle section of the curve is now very small (of the order of 10^{-2} mm) and that the region CB (in figure 4, B represents oxygen concentration, A that of phosphorus), limited by the straight line C, according to the equation

$$\frac{p_{P_4}}{p_{O_2}^m} = \text{const.},$$

is very narrow.

Conversely we may conclude that the phenomenon of the minimum or maximum critical pressure of one of the components is a peculiar property of all explosive mixtures and that therefore its theoretical interpretation is of far reaching importance. In this laboratory, besides phosphorus, the inflammation of sulfur (14) has also been investigated. Here, similarly, the existence of a minimum as well as a maximum pressure of oxygen has been observed. It was found furthermore that sulfur vapor can be burned in oxygen at temperatures even considerably below 100° . Therefore, the statement, frequently found in text-books, that the inflammation temperature of sulfur is 285° , is somewhat misleading. This temperature is significant only in that respect that the vapor pressure of sulfur reaches here a value for which the upper critical pressure of oxygen becomes equal to one atmosphere. At pressures below atmospheric the combustion can go at much lower temperatures. However, below 100° no spontaneous inflammation usually occurs, even with pressures within the explosion interval. But, as was mentioned previously, immeasurably small traces of ozone cause inflammation in this temperature range.

Sagulin (2) and also Garner and Gomm (15) have found that mixtures of carbon monoxide and oxygen explode at a minimal

⁷ The law of the residual pressure $p_r p_{p_4}^m = \text{const.}$ can be written thus:

$$p^I + m = \frac{\text{const.}}{\gamma (1 - \gamma)^m}.$$

where p is the total pressure, $p_r = \gamma p$ and $p_{p_4} = (1 - \gamma) p$.

pressure p_{\min} of the order of a few centimeters and that this pressure increases very slowly from 20 to 30 mm. when the temperature is decreased from 736 to 578°. However, there exists a critical temperature T_k below which at no pressure does an explosion occur. Sagulin and the writer have recently studied

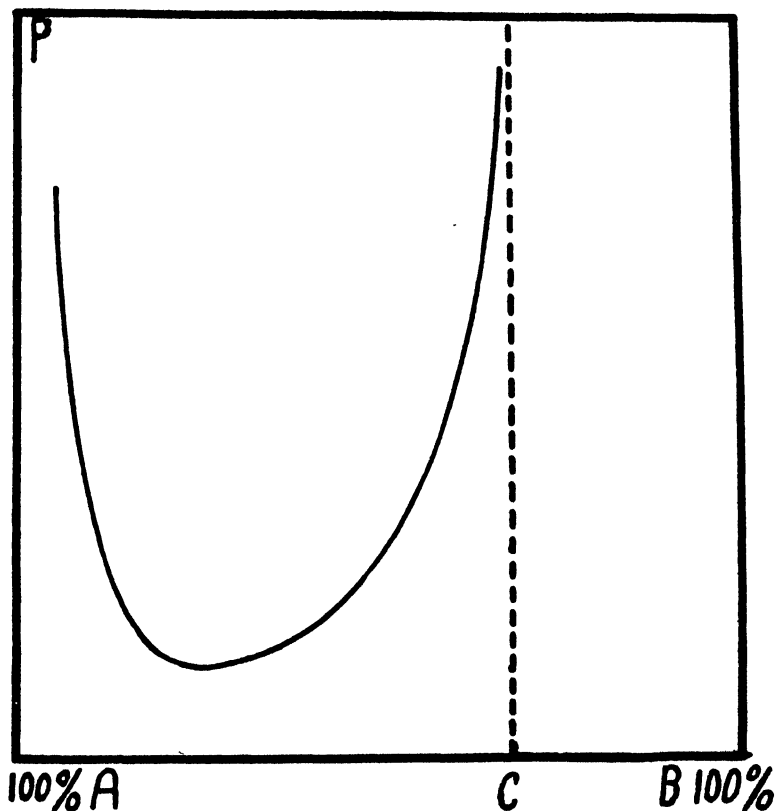


FIG. 4. EXPLOSION PRESSURE AS A FUNCTION OF COMPOSITION

more in detail the significance of this critical temperature. It was found that above the critical temperature an explosion occurs only within certain limits of the pressure of the mixture—from a p_{\min} to a well defined p_{\max} . The composition of the mixture has very little influence on these pressures. The relation experimen-

tally obtained between the critical pressure and the temperature is indicated on figure 5. The explosion is possible only within the area bounded by the curve ABC. The value of p_{\max} varies with temperature, changing from 60 mm. at 570° to 380 mm. at 683° . A sufficient further increase of the pressure should change this explosion finally, as can be deduced theoretically, into a thermal

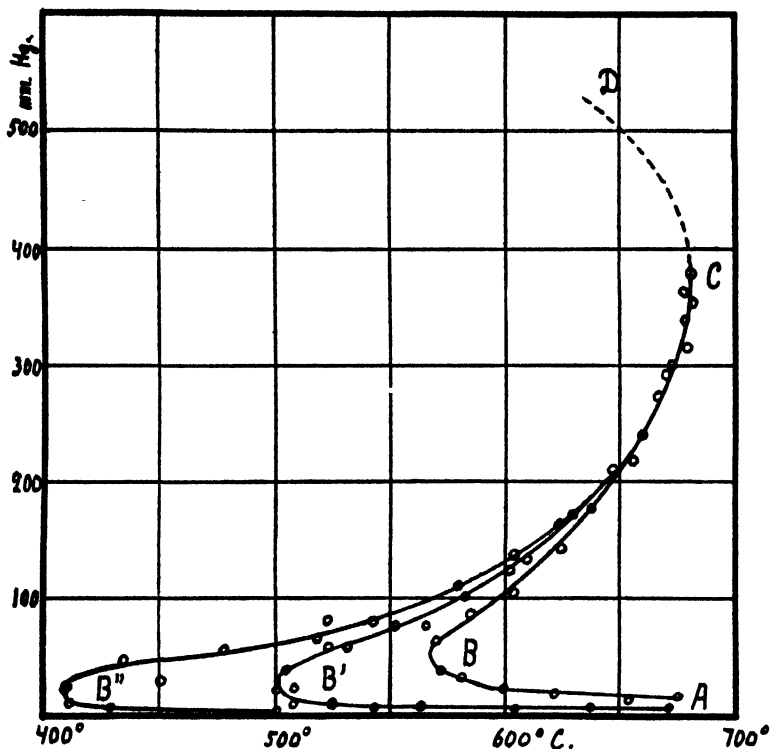


FIG. 5. EXPLOSION PRESSURE-TEMPERATURE RELATION FOR CO + O₂ MIXTURES

explosion. The critical pressure of this latter is indicated on figure 5 by the dotted line, CD following from the equation (1)

$\log p = \frac{A}{T} + MB$, with a large A , thus with a very high heat of activation, which is more than probable for the carbon monoxide-oxygen reaction. If this suggestion is correct, the complete

region of explosion is bounded by the curve ABCD. It is remarkable that an addition of even immeasurably small amounts of NO ($\sim 10^{-5}$ mm.) extends the explosion region to considerably lower temperatures, increasing the upper and decreasing the lower critical pressure as shown by the curve AB'C of figure 5.

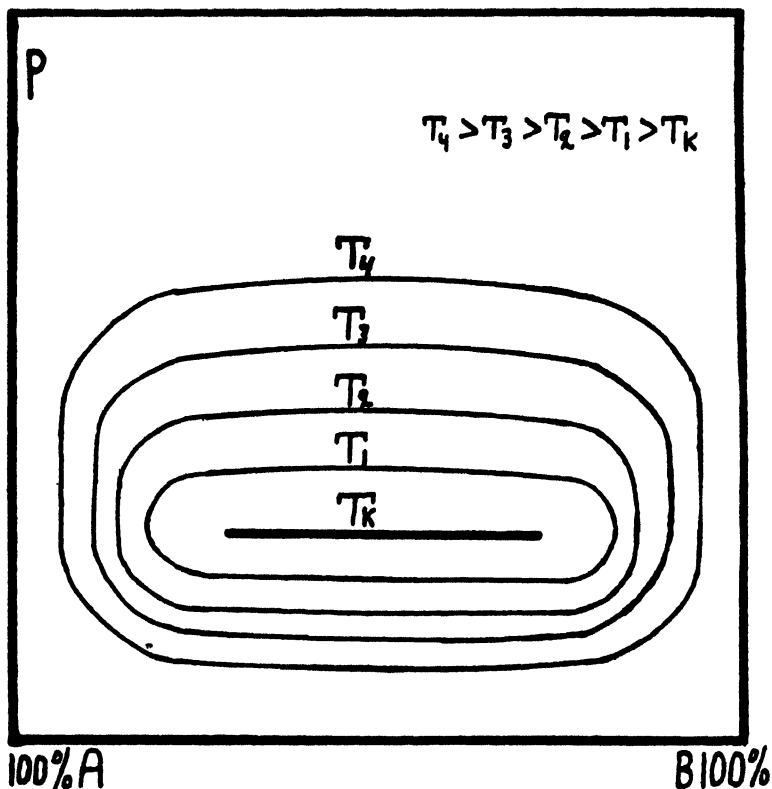


FIG. 6. EXPLOSION PRESSURE AS A FUNCTION OF COMPOSITION FOR CO + O₂ MIXTURES

Measurable quantities of NO (0.5 to 1.0 mm.) decrease the limiting T_k by almost 200° (the curve AB'C on figure 5.). The measurement of p_{\max} has been carried out by us in the following manner: 1. On introducing the carbon monoxide-oxygen mixture at a pressure larger than p_{\min} and at a temperature lower than

T_k , the vessel is slowly warmed up.⁸ At some temperature T_1 , an explosion occurs, and this temperature was found to be the higher, the higher was the pressure of the reacting mixture.

2. After warming up the vessel to some temperature $T > T_k$, it is rapidly filled by the gas mixture to a pressure $p > p_{\max}$; the inflammation which starts when the pressure becomes larger than p_{\min} is extinguished when $p > p_{\max}$. Afterwards the gas mixture is passed slowly through the vessel and the pressure is gradually reduced. At some pressure an explosion occurs and this pressure is the desired p_{\max} .

Both these methods gave results in good agreement.

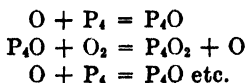
It should be pointed out here that the effect of the maximum total explosion-pressure of the carbon monoxide-oxygen mixtures and the existence of the maximal partial pressure of oxygen in phosphorus combustion, are quite different phenomena. Representing the data for $\text{CO} + \text{O}_2$ reactions in a diagram of the same type as figure 4, one obtains figure 6, in which the explosion region is enclosed by the curves drawn for the successively increasing temperatures $T_k < T_1 < T_2$ etc.

Considering the theory of the phenomena described one must remember that the reaction velocity $w = \frac{n}{1 - \alpha}$ becomes infinite when $\alpha = 1$. Nevertheless, in the case of sulfur vapor, even when the condition $\alpha > 1$ is fulfilled, an inflammation occurs only when traces of ozone are introduced. The only reasonable explanation of this last effect is the following: the reaction is started by oxygen atoms, which, at these temperatures, cannot be formed spontaneously (that is by thermal activation) on account of the very large energy of dissociation of O_2 involved. Therefore $n = 0$. But when $n = 0$, no matter how large α is, the reaction cannot develop. It suffices however to introduce artificial reaction centers (the dissociation $\text{O}_3 = \text{O}_2 + \text{O}$ for instance requires much less energy than $\text{O}_2 = 2\text{O}$.) to obtain a finite n , even though it may be small. Once the reaction is started and $\alpha > 1$, the

⁸ The thermal reaction below the explosion point is very slow.

rate will be autocatalytically accelerated, until an inflammation occurs.

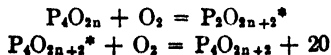
In the case of the burning of phosphorus vapor the reaction centers are formed spontaneously. It is nevertheless likely that in this reaction as well, the reaction centers are oxygen atoms. The difference in behavior in comparison with sulfur may be attributed to a very slow but probable reaction with solid phosphorus in which oxygen atoms are produced. The mechanism of the gaseous reaction can be written thus:



Assuming that the chains are broken on the walls, the probability of breaking a chain is $\beta_0 = \frac{1}{\nu_0}$ where ν_0 is given by (12)

$$\nu_0 = \frac{6 \pi d^2}{4 \lambda_0^2} [\text{P}_4] [\text{O}_2] \left(1 + \frac{[\text{A}]}{[\text{P}_4] + [\text{O}_2]} \right) \quad (16)$$

The mechanism of the phosphorus reaction suggested above includes only the main chain. But there is a possibility of the chains branching owing to the consecutive reactions of P_4O_2 to form finally P_4O_{10} :



The asterisk indicates here an excess internal energy. The second of the reactions can occur only when the kinetic energy of the oxygen molecules O_2 , together with the excess energy φ_2^* of the $\text{P}_4\text{O}_{2n+2}$ molecule, exceeds 160,000 cal. Denoting the difference $160,000 - \varphi = U$ we find that the probability of this secondary activation is $e^{-U/RT}$ and according to the equation (14) the condition of inflammation is expressed by $\beta_0 - 2 e^{-U/RT} = 0$, therefore:

$$\frac{6 \pi d^2}{4 \lambda_0^2} [\text{P}_4] [\text{O}_2] \left(1 + \frac{[\text{A}]}{[\text{P}_4] + [\text{O}_2]} \right) = 2 e^{+U/RT} \quad (16a)$$

or, at a constant temperature:

$$d^2 [P_d] [O_2] \left(1 + \frac{[A]}{[P_d] + [O_2]} \right) = \text{constant} \quad (16b)$$

This is the same expression as one obtained experimentally (equation 15, p_r of equation (15) is now expressed as $[O_2]$). Even

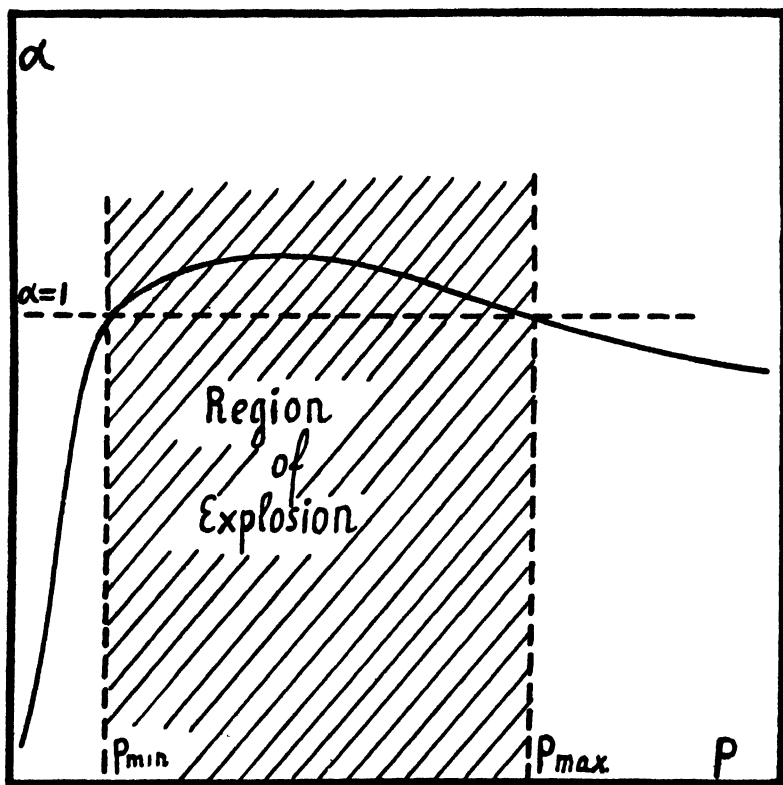


FIG. 7. α AS A FUNCTION OF PRESSURE

more, the theory enables one to compare the theoretical residual pressure with the experimentally determined value. The experiments have shown that p_r is independent of temperature. Taking into account the probable error of this determination it can be shown that the magnitude $e^{-U/RT}$ of equation (16a) does not exceed 0.1 at room temperature. The magnitude of λ_0 is known,

so that from equation (16b) the theoretical residual pressure ($[O_2]$ or p_r) can be easily calculated. Values thus obtained agree within a factor of two with the experimentally determined values.⁹ Going over now to the phenomenon of the maximal critical pressure one is forced unfortunately to concede that at present the

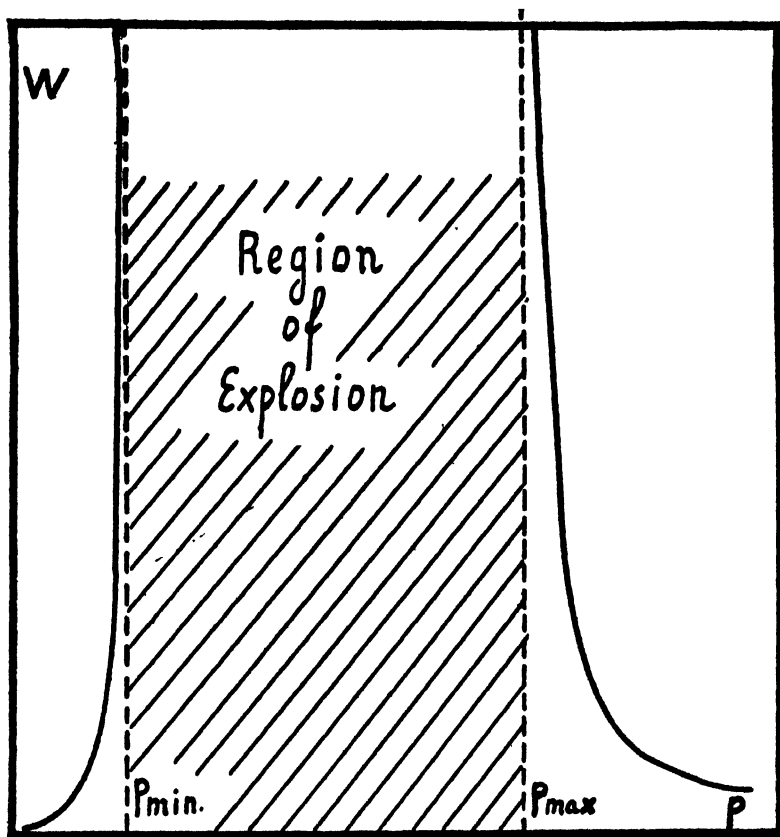


FIG. 8. REACTION RATE AS A FUNCTION OF PRESSURE

theory of this effect is not as certain. The chain theory, however, indicates at least a general direction along which the explanation should be sought. The magnitude of α , as a function of the partial pressure of oxygen, judging from experimental data in the

⁹ See the forthcoming article in *Z. physik. Chem., Abt. B.*

phosphorus reaction, has apparently the shape represented in figure 7; it has thus a maximum $\alpha > 1$ and cuts in two points the ordinate $\alpha = 1$. Assuming such a relation for α , the reaction rate as a function of oxygen pressure will be represented by figure 8.

Why α decreases again when the pressure of oxygen exceeds some value is difficult to answer definitely. It is possible, however, that oxygen contains some impurity reacting with oxygen atoms and thereby breaking the chains. The concentration of this impurity $[R]$ must be proportional to the concentration of oxygen: $[R] = \mu [O_2]$, the coefficient μ being probably very small. In a case of this type the ordinary probability of breaking a chain must be increased by the probability of an oxygen atom reacting with the impurity and thus also ending the chain. Therefore, instead of the expression:

$$w = \frac{n}{1 - \alpha} = \frac{n}{\frac{1}{\nu_0} - e^{-U/kT}}$$

one obtains:

$$\frac{1}{\nu_0} - e^{-U/RT} + \frac{\mu [O_2]}{\mu [O_2] + [P_4]} \quad (17)$$

where $e^{-U/RT}$ is of the order of 0.1. When the pressure of oxygen is small, the third term of the denominator is very small also and can be therefore neglected. Thus the condition $\frac{1}{\nu_0} - 0.1 = 0$, still determines the minimal critical pressure of oxygen. For large oxygen pressures $\frac{1}{\nu_0}$ becomes negligibly small but instead

$f = \frac{\mu [O_2]}{\mu [O_2] + [P_4]}$ grows. At some $[O_2]_{\max}$ when $f > 0.1$ the inflammation becomes impossible again. The condition determining the maximal oxygen pressure is therefore:

$$\frac{\mu [O_2]_{\max}}{\mu [O_2]_{\max} + [P_4]} = 0.1$$

from this follows:

$$[\text{O}_2]_{\max} = \frac{0 \cdot 1 [\text{P}_4]}{1 \cdot 1 \mu} \quad \text{or} \quad \frac{[\text{O}_2]_{\max}}{[\text{P}_4]} = \frac{0.09}{\mu} = \text{const.}$$

Thus the direct proportionality between $[\text{O}_2]_{\max}$ and $[\text{P}_4]$ in accordance with experimental results is obtained. The experimentally determined ratio of oxygen to phosphorus pressure was of the order of 10^4 , thus μ is of the order of 10^{-5} and the concentration of the assumed impurity in oxygen need not be larger than 0.001 per cent. In favor of this explanation of the maximal pressure is the observation frequently made that the maximal pressure is very sensitive to the presence of traces of foreign substances. Several observations of this character have been made in this laboratory also.

The reaction theory here presented accounts not only for the two limiting cases (chains stopped exclusively on the walls or exclusively in the gas phase) but, when considered more in detail, also for the transition region, in particular for the experimental observation (see figure 3) that a lower pressure of phosphorus vapor exists below which at no oxygen pressures an explosion occurs. To show this we rewrite now the condition of explosion (from 17)

$$\frac{I}{\nu_0} - e^{-U/RT} + \frac{\mu [\text{O}_2]}{\mu [\text{O}_2] + [\text{P}_4]} = 0, \quad (18)$$

using for ν_0 the value given by expression (16) in absence of an inert gas: $\nu_0 = \text{Cd}^2 [\text{P}_4] [\text{O}_2]$, substituting: $e^{-U/RT} = a$ and assuming $\mu [\text{O}_2] < [\text{P}_4]$, thus

$$\frac{I}{\text{Cd}^2 [\text{P}_4] [\text{O}_2]} - a + \frac{\mu [\text{O}_2]}{[\text{P}_4]} = 0, \quad (18a)$$

Introducing further $\frac{I}{\text{Cd}^2 a} = k_1$, and $\frac{\mu}{a} = k_2$ one obtains

$$k_1 [\text{O}_2]^2 - [\text{P}_4] [\text{O}_2] + k_2 = 0, \quad (18b)$$

an equation which yields as solutions:

$$[O_2]_{\min} = \frac{[P_4] - \sqrt{[P_4]^2 - 4 k_1 k_2}}{2 k_2} \quad (19)$$

$$[O_2]_{\max} = \frac{[P_4] + \sqrt{[P_4]^2 - 4 k_1 k_2}}{2 k_2} \quad (19a)$$

Equations (19) and (19a) give, for the condition: $[P_4]^2 > 4 k_1 k_2$ the experimentally obtained limiting expressions:

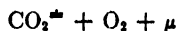
$$[O_2]_{\min} = \frac{k_1}{[P_4]} \quad \text{and} \quad [O_2]_{\max} = \frac{[P_4]}{k_2}$$

and show in addition that a critical phosphorus vapor pressure $[P_4]^2 = 4 k_1 k_2$ exists, below which the root becomes imaginary, thus an explosion becomes impossible at any oxygen pressures. It may be added that the simplification $\mu [O_2] < [P_4]$ made above in order to arrive to expressions (19) and (19a) does not change the conclusions reached here, although it simplifies very materially the calculations.

The existence of the maximal total pressure in the combustion of carbon monoxide is more difficult to interpret. The theory cannot be based upon the inhibiting action of some impurity because the expression $\frac{[O_2]}{[O_2] + [CO]}$ is independent of total pressure for a given composition of the gas. It is noteworthy that substitution of air instead of oxygen gives the same value for the maximal pressure p_{\max} of inflammation (by p_{\max} is meant here the total pressure $[CO] + [O_2] + [N_2]$). All this indicates rather some physical than chemical cause of the phenomenon. One might consider, for instance, the following reaction scheme:



(The occurrence of the second reaction requires approximately 10,000 calories additional activation energy of O_2). A triple collision of the type:



in contradistinction to reaction (2) may result in no formation of oxygen atoms, these recombining immediately and the energy being transferred to μ (this being some other, not further defined molecule). Such a mechanism gives the desired explanation but since no experimental evidence is available at present further discussion appears unjustified. The only conclusion that can be drawn is that a higher concentration of molecules facilitates somehow the breaking of the chains, the probability of this happening increasing with pressure. Such assumption will lead to a relationship between p and T of the same type as was obtained experimentally in the combustion of carbon monoxide.

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MOLECULAR ASSOCIATION¹

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INTRODUCTION

More than fifty years ago, Louis Henry first proposed the hypothesis of molecular polymerization, now called molecular association. Then successively, Vernon, Eötvös, Ramsay-Shields Trouton, Ph. A. Guye, Daniel Berthelot, Traube, Longinescu, Vaubel, Walden, Bingham and others published methods for determining the degree of molecular association, particularly for liquids. The experimental and theoretical material thus collected can not be disregarded but the question is far from the state of perfection now attained by the theory of electrolytic dissociation, founded in 1887, ten years after Henry's first paper, by Svante Arrhenius.

Solids, liquids and even certain gases are supposed to be composed of simple, double, triple, etc., molecules. So also water may be an extraordinarily complex liquid, formed by the accumulation of multiple molecules up to hextuples, and named dihydron, trihydron, tetrahydron, pentahydron and hexahydron, whose constitutional formulas have the form of a triangle, square, pentagon or hexagon, similar to the formulas of the saturated cyclic hydrocarbons, but with oxygen occupying the place of the carbon atom (Armstrong). Tamman has attempted to calculate the proportions of these complex molecules. In spite of all attempts, not a single type of these molecules has been isolated. To explain this failure, a new hypothesis has been added, namely, that associated molecules are in unstable equilibrium, so that they dissociate and come together again with great rapidity. To explain one hypothesis by another is hardly a method of finding the de-

¹ Translated from the French by Marion Hull.

sired truth. In recent years experimental proof that there is a molecular accumulation in crystals has been adduced with the aid of x-ray spectra (Bragg). Yet there is no satisfactory agreement between values for the degree of molecular association found by different methods. All this proves clearly that the hypothesis of molecular association, of molecules attached to each other, should be replaced by an idea which is nearer to reality.

For this reason G. G. Longinescu and G. Chaborski consider molecular association as a phenomenon of molar concentration. In place of molecular complexity they introduce the idea of molecular accumulation, and instead of degree of association that of degree of molecular accumulation. Water, the liquid which shows the highest degree of molecular association, has the greatest molar concentration, i.e., 55.5, and consequently the highest degree of accumulation. According to this point of view liquids, like gases, consist solely of simple molecules. The more a liquid is associated, the greater the number of these molecules in equal volumes. In numerous cases the degree of molecular association is approximately one-tenth of the molar concentration. The degree of accumulation X is equal to $100 \times D/M$. Thus for water the degree of accumulation is $100 \times 1/18 = 5.55$.

For thirty years I adhered to the general but erroneous theory of molecular association in spite of the vain attempts to harmonize the values for the degree of molecular association found by different methods. The credit for permanently changing my outlook belongs to my pupil and collaborator, Dr. Gabriela Chaborski, lecturer in inorganic chemistry at the University of Bucharest. It is significant that the great Dutch scientist, Van der Waals, combatted the theory of molecular association for more than thirty years and began to believe in it only towards the end of his life (Turner).

THE WORK OF LOUIS HENRY

Louis Henry, for fifty years professor of chemistry at the Catholic University of Louvain, published more than four hundred memoirs, a great number of which are on the relation between the volatility and the chemical constitution of organic compounds.

His first article on polymerization was published in 1878 (1). Twenty-seven years later he returned to these same ideas, "older really than 1878" (2). It is impossible, except by reprinting his work or by extensive quotation, to make amends to this Belgian chemist for the injustice done to him in the past, for scarcely an author mentions his work though it forms the basis of one of the most important chapters in modern physical chemistry. True, his ideas were primarily philosophical and qualitative, and he gave no precise values for the degree of molecular association. Yet they underlie modern progress in the same way that the work of Avogadro and the philosophic ideas of Crookes, Stokes and Lord Kelvin laid the foundations for our present knowledge of atomic structure. Henry deserves recognition for ideas which were prophetic half a century ago but are now universally accepted.

The starting point of his theory was the striking difference between the melting and boiling points of oxides and chlorides which are apparently similar in chemical composition. Even today a large proportion of the methods for determining molecular association are directly dependent on the differences between the melting and boiling points of normal and associated compounds, though numerous other physical constants, such as the surface tension, viscosity, molecular refraction and internal pressure, are also used. Henry explained the volatility of the chlorides, as compared with the oxides,—in the face of a greater volatility of oxygen as compared with chlorine,—on the assumption that the metallic oxides are in reality polymers of the unit MO . He assumes that the formulas of the chlorides are generally deduced from the vapor densities and are properly speaking molecular formulas, expressing the size and true weight of the molecules, while similar formulas for the oxides are minimal only. The following quotation presents the basis of his studies on oxides:

Most of the molecular formulas in use relate to the perfect gaseous state; they are insufficient for many compounds and inapplicable to the various states through which the same compound can pass artificially. Such are the formulas which are generally given to metallic oxides. They represent neither the true nature of these compounds, nor the true

size of their molecule. The metallic oxides RO_x , really similar to the chlorides, are for the most part unknown to us. We know only the very complex polymers $(\text{RO}_x)_n$ where n represents a high figure. As proof of this fact, can be cited the adding power of the oxides, their preparation by extremely complex progressive dehydration of hydroxides, occasioning a true molecular condensation, and finally their density in the solid state, which is abnormal in comparison with that of the corresponding hydroxides.

Shall we ever succeed in preparing or discovering the normal oxides, of which we know only such uncommon examples and which must be, in general, so different in properties from our present oxides? I do not know. All I can state is that in order to prepare them the conditions must be entirely different from those in which we are working today, for our present mode of preparing oxides is the sum total of all the circumstances under which these unknown compounds polymerize and escape us.

Twenty-seven years later, Louis Henry returned to these same ideas with more detail and precision, in his report, *L'État moléculaire de l'eau*, parts of which are quoted below:

Formed from two perfect gases, the one, H boiling at -253° under one atmosphere of pressure, the other O at -184° , uniting with a contraction of only a third of their volumes, liquid water boils at 100° and constitutes a truly exceptional case from the physical point of view. Its extraordinary characteristics are more easily recognized if we recall its congener, hydrogen sulfide, H_2S , which although containing sulfur, a solid boiling at 444° , is a gas boiling at about -61° . According to the best established analogies water should naturally be gaseous and should have a boiling point considerably below zero on the thermometric scale. According to Forcrand it should be in the neighborhood of -65° .

This anomaly Henry attributes to the metallic character of hydrogen which, as in other metallic oxides, produces polymerization, the latter being responsible for the values of the physical constants of liquid water. At the same time Henry considers water to be a symmetrical oxide, whose two hydrogens are identical, rather than an asymmetric hydroxyl compound, whose polymerization might be due to the hydroxyl radical as is presumably

the case in alcohols and acids, the most highly polymerized of organic compounds.

VERNON'S METHOD FOR DEGREE OF MOLECULAR ASSOCIATION

Early in 1891, Vernon published the first numerical data on the degree of molecular association (3). By comparing the boiling points of different organic compounds, Vernon found that doubling the molecular weight raises the temperature of boiling about 100° . Thus, while ethylene boils at -105° , butylene boils at -5° , octylene at $+126^{\circ}$, and hexadecylene at $+274^{\circ}$. The boiling point of water is 200° high because it is in reality four times associated. Hydrofluoric acid boils at 19.4° instead of -140° , hence its formula must be between $(\text{HF})_2$ and $(\text{HF})_4$. In the same way, liquid sulfur has the molecule, S_{12} . Sulfur dioxide, phosphorous trichloride and carbon tetrachloride are normal, nitric acid is twice polymerized and sulfuric acid four times. These values, determined by Vernon, are qualitative; sometimes they approximate the values found by other methods, but often they differ from them.

THE FORMULAS OF G. G. LONGINESCU

Ten years later, in 1901, we published our memoir "Observations sur les températures d'ébullition de quelques corps organiques liquides" (4). In this article, we showed the connection between the boiling points of organic liquids and their chemical composition. The principles which we followed in the investigation of this relationship were the ideas that the boiling point of a liquid must depend on its molecular weight, the number of molecules in unit volume, the number of atoms in a molecule and the nature of these atoms. To simplify the solution of such an involved problem, we divided it into four parts. In the first place, we compared the boiling point (on the absolute scale) of two liquids having the same number of molecules in unit volume ($D:D' = M:M'$) and the same number of atoms in a molecule, compounds containing C, H, O and N, elements having atomic weights up to 35.5. For these compounds the relation between

boiling points is almost equal to the ratio of their molecular weights.

In the second place, to determine the influence of the number of molecules in unit volume, we compared compounds for which the ratio of the densities is not proportional to the ratios of the molecular weight, but which always have the same number of atoms in each molecule. We found in this case that the ratio of the boiling points is equal to the ratio of the densities. Since the density of a compound is equal to the product of the molecular weight times the number of molecules in a unit volume, the boiling point of an organic substance is proportional both to the molecular weight and to the number of molecules.

In the third place, to establish the influence of the number of atoms contained in the molecule, we compared two compounds of different densities, having also a different number of atoms. In this case the ratio of the temperatures becomes equal to the ratio of the densities multiplied by the square root of the ratio of the number of atoms.

Denoting by T and T' the absolute boiling points, by M and M' the respective molecular weights, by N and N' the respective number of molecules in unit volume and by n and n' the number of atoms in these molecules, we can represent the above results by the formula:

$$\frac{T}{T'} = \frac{M}{M'} \frac{N}{N'} \sqrt{\frac{n}{n'}}$$

Since 1901, this formula has been mentioned in various physical and chemical treatises, of which we will mention the one by O. D. Chwolson (5).

THE DEGREE OF MOLECULAR ASSOCIATION OF ORGANIC COMPOUNDS IN THE LIQUID STATE

Two years later, in 1903, (6), we expressed this relation in the following form:

$$\frac{T}{D \sqrt{n}} = \frac{T'}{D' \sqrt{n'}} = \text{a constant}, \quad (1)$$

which is the starting point for a new method for the more exact determination of the degree of association of organic compounds in the liquid state. For a greater number of compounds the value for the constant is about 100. For compounds whose molecules are associated, like alcohols, acids, nitriles, etc., its value is much greater than 100, attaining the maximum value of 215 for water. From the relation (1) we can deduce:

$$\left(\frac{T}{100 \times D}\right)^2 = n \quad (2)$$

by placing the constant = 100. This relation permits the calculation of the number of atoms in a molecule of an organic liquid. In table 1, we give the number of atoms calculated in this way for a considerable number of compounds along with the known number of atoms in the same molecule. The table shows that the difference between these two figures is two units at the most. This insignificant difference shows us that the compounds considered are not polymerized. In table 2 are included the two numbers for compounds which are positively polymerized. According to our point of view, the degree of association is the ratio between n calculated and n known.

There is a remarkable agreement between the degree of association according to our method and that obtained by Ramsay-Shields and others. In particular, our value for the degree of association of water, 4.6, is close to that of Ramsay, 3.8, and that of Vernon, 4. Nitriles, alcohols and acids polymerize and appear to be wholly distinct from normal compounds.

THE DEGREE OF ASSOCIATION OF ORGANIC SUBSTANCES IN THE SOLID STATE

It is interesting to question whether a relation analogous to the preceding is possible for solid compounds. It would cast light on the obscure problem of physical chemistry as to whether solid compounds also exhibit the phenomenon of molecular polymerization.

TABLE I
The number of atoms in organic molecules

NAME OF COMPOUND	n		NAME OF COMPOUND	n	
	Calculated	Known		Calculated	Known
Methylene chloride.....	5	5	Benzyl chloride.....	16	15
Acetyl chloride.....	8		Ethyl hydroxyacetate .	16	15
Methyl monochloroformate... 8			Dimethylfuran.....	16	15
Ethylene chloride.....	8		Anisole.....	18	16
Methyl formate.....	9		Butyl nitrate.....	15	17
Methyl nitrate.....	8		Ethyl monochloropropionate.	15	17
Ethyl chloride.....	9		Amyl chloride.....	18	17
Thiophene.....	10		Indene.....	18	17
Epichlorohydrin.....	10		Ethyl propionate.....	16	17
Ethyl nitrite.....	9		Methyl butyrate.....	17	17
Propionyl chloride.....	11		Propyl monochloroacetate....	16	17
Ethyl nitrate.....	10		Propyl acetate.....	17	17
Ethyl sulfonyl chloride.....	10		Butyl formate.....	17	17
Ethyl monochloroformate.... 10—			Piperidine.....	18	17
Methyl monochloroacetate... 10			Ethenylaminophenol.....	17	17
Methyl dichloroacetate..... 9			α -Chloronaphthalene.....	19	18
Furfural.....	12		Acetylphenol.....	18	18
Propyl chloride.....	12		Methyl propyl carbonate....	16	18
Methyl acetate.....	12		Hexahydrobenzene.....	18	18
Methyl carbonate.....	13		Ethyl carbonate.....	17	18
Chlorobenzene.....	12		Methyl benzoate.....	18	18
Allyl nitrate.....	12		Ethyl propyl ether.....	20	18
o-dichlorobenzene.....	12		Ethyl lactate.....	17	18
Methyl hydroxyacetate.....	13		Propyl hydroxyacetate.....	18	18
Butyryl chloride.....	14		Ethyl sulfocarbonate.....	18	18
Methyl sulfate.....	12		Ethyl sulfite.....	16	18
Methyl monochloropropion- ate.....	14		Ethyl sulfate.....	17	19
Ethyl monochloroacetate.... 14			Propionic anhydride.....	19	19
Methyl monochloroformate... 13			Cresol methyl ether.....	20	19
Benzol chloride.....	14		Ethyl phenyl ether.....	20	19
Ethyl acetate.....	14		Ethyl acetylacetate.....	18	19
Butyl chloride.....	14		α Methylpiperidine.....	20	20
Propyl nitrate.....	14		Ethyl butyrate.....	19	20
Methyl ethyl carbonate.....	14		Butyl acetate.....	19	20
Ethyl acrylate.....	15		Hexyl chloride.....	19	20
Methyl lactate.....	14		Methyl valerate.....	19	20
Ethyl ether.....	17		Ethyl benzoate.....	20	20
Chlorotoluene.....	16		Ethyl oxalate.....	18	20
			α Isopropylpyridine.....	21	20

TABLE 1—*Concluded*

NAME OF COMPOUND	<i>n</i>		NAME OF COMPOUND	<i>n</i>	
	Calculated	Known		Calculated	Known
n, Propylbenzene	23	21	Thymol methyl ether	26	27
Benzyl acetate	20	21	Butyl sulfide	28	27
Allylaniline	23	21	Heptyl methyl ether	28	27
Propyl ether	23	21	Methyldiphenylamine	28	27
Hexahydrotoluene	23	21	Decahydronaphthalene	29	28
Ethyl propyl carbonate	19	21	Methyl hexyl ketone	30	28
Ethyl methylacetoacetate	21	22	Octylamine	30	28
Triethylamine	23	22	Tetraethylsilicane	27	29
Allyl benzoate	23	22	Amyl butyrate	27	29
Tetrahydronaphthalene	23	22	Methone	28	29
Phenyl sulfide	25	23	Heptyl acetate	28	29
Heptyl chloride	23	23	Hexahydrocymene	29	30
Butyl propionate	22	23	Octyl methyl ether	31	20
Paraconine	24	24	Methyl octyl ketone	33	31
Triethylsilicol	24	24	Octyl acetate	30	32
Triethylcarbinol	23	24	Heptyl propionate	30	32
Propyl carbonate	22	24	Decane	33	32
Acetylnaphthol	24	24	Triphenylamine	31	32
Pentyl ethyl ether	25	24	Amyl ether	31	33
Butylbenzene	26	24	Phenyltriethylsilicane	31	33
Carvacrol	26	24	Octyl ethyl ether	33	33
Butyric anhydride	23	25	Undecane	37	35
Butyl phenyl ether	26	25	Octyl propyl ether	36	36
Ethyl cinnamate	26	25	Dodecane	40	38
Terebene	25	26	Octyl butyl ether	38	39
Conine	27	26	Tributylamine	38	40
Propyl valerate	25	26	Tridecane	43	41
Ethynaphthalene	24	26	Tetradecane	46	44
Diethylaniline	27	26	Octyl ether	49	51

The first point to settle is that relating to the value of the constant in the formula. As a result of comparisons, which we made, this constant may have a value of 50 or of 70.

Table 3 contains values of *n* for the solid state, calculated with the aid of the formula:

$$\left(\frac{T}{70 \times D} \right)^2 = \quad (3)$$

TABLE 2
The number of atoms in polymerized organic molecules

NAME OF COMPOUND	n		NAME OF COMPOUND	n	
	Calculated	Known		Calculated	Known
Formic acid.....	9	5	Propylamine	20	13
Acetonitrile.....	19	6	Isopropylamine.....	21	13
Methyl alcohol.....	19	6	Trimethylene alcohol.....	21	13
Methylcarbylamine.....	13	6	Propylene alcohol.....	20	13
Acetaldehyde.....	14	7	Phenol... ..	18	13
Thioacetic acid.....	13	8	Thiophenol	17	13
Propargyl alcohol.....	16	8	Trimethylamine	17	13
Acetic acid.....	14	8	Chlorhydrin	18	13
Propionitrile	21	9	Aniline.....	19	14
Ethyl alcohol.....	19	9	Butyric acid.....	19	14
Allyl cyanide.....	21	9	Benzaldehyde.....	18	14
Ethylcarbylamine	21	9	Butyl cyanide	26	15
Ethylene cyanohydrin	22	10	Ethylacetamide.....	26	15
Allyl alcohol.....	18	10	Butyl alcohol	22	15
Glycol.....	17	10	Benzyl cyanide	25	16
Acetone	16	10	Butylamine.....	21	16
Ethyl thiocyanate	16	10	Diethylamine.....	20	16
Dimethylamine.....	17	10	Diethyl ketone	20	16
Ethyl amine.....	16	10	Benzyl alcohol	20	16
Nitroethane	14	10	Methyl propyl ketone	20	16
Propyl aldehyde.....	14	10	Butyl thiocyanate	21	16
Allyl sulfocyanate.....	16	11	Methyl aniline	23	17
Pyridine.....	16	11	Valeric acid.....	23	17
Propionic acid.....	17	11	α Quinoline.....	22	17
Propyl cyanide.....	24	12	Benzylamine.....	21	17
Ethylformamide.....	23	12	Amyl cyanide	27	18
Propyl alcohol.....	20	12	Methyl butyl ketone.....	24	19
Phenyl cyanide.....	21	13			

in which T is the melting point of the solid organic compound and D its density in the solid state. The values of n thus calculated with $C = 70$, approximate those which are known. In the third column of this table are the values obtained for n in the liquid state, calculated with the help of the density in the solid state, the boiling point and the constant $C = 100$. By the close cor-

TABLE 3
The number of atoms in the molecules of organic solids

NAME OF COMPOUND	n KNOWN	n CALCULATED		NAME OF COMPOUND	n KNOWN	n CALCULATED	
		Solid	Liquid			Solid	Liquid
m-aminobenzoic acid.....	17	17	—	Cinnamyl methyl ketone..	21	19	26
Anisic acid.....	19	21	—	Cumidine.....	23	25	28
Acetopropionic acid.....	16	15	20	p-Chlorophenol.....	13	12	15
Camphoric acid.....	30	29	—	β -Chloronaphthalene.....	18	14	18
Cinnamic acid.....	19	20	20	+ Camphor.....	26	28	24
Citric acid.....	21	21	—	Dimethylaniline.....	20	17	23
Citramalic acid.....	18	15	—	Erythritol.....	18	15	15
Cumic acid.....	24	23	—	p-phenylquinoline.....	26	22	—
Phthalic acid.....	18	18	—	Guyaiacol.....	17	17	16
Phenylacetic acid.....	18	17	18	α Naphthol.....	19	18	21
Gallic acid.....	18	17	—	β Naphthol.....	19	23	—
Hippuric acid.....	23	25	—	Nitrobenzene.....	14	11	16
Itaconic acid.....	15	15	—	σ -Nitrophenol.....	15	15	17
Maleic acid.....	12	13	—	p-Nitrophenol.....	15	15	—
Amygdalic acid.....	19	17	—	Naphthalene.....	18	18	18
Malic acid.....	15	12	—	σ -Nitroaniline.....	16	15	15
Methylsuccinic acid.....	17	15	—	p-Nitroaniline.....	16	17	—
m-nitrobenzoic acid.....	17	17	—	o-Nitrochlorobenzene....	14	10	14
Oxalic acid.....	8	10	—	m-Nitrochlorobenzene....	14	10	14
Protocatechuic acid.....	17	18	—	p-Nitrochlorobenzene....	14	14	14
Salicylic acid.....	16	18	—	+ m-Nitrotoluene.....	17	12	18
Succinic acid.....	14	16	—	+ p-Nitrotoluene.....	17	18	20
Tetrahydrobenzoic acid..	19	16	22	+ 1, 2, 4, Nitroxylenes...	20	15	22
Trichloroacetic acid.....	8	9	8	Orcinol.....	17	16	18
Tartaric acid.....	16	14	—	Methyl oxalate.....	14	16	14
Phthalic anhydride.....	14	14	14	Phenanthraquinone.....	24	24	—
Acetanilide.....	19	20	21	Pyrogallol.....	15	15	14
Acetocinnamone.....	21	20	—	Pyrocatechol.....	14	15	14
Acetophenone.....	17	18	—	Saligenin.....	17	19	—
Aniline.....	14	13	18	p-toluidine.....	17	18	19
Benzamide.....	16	18	17	Thymol.....	25	22	—
Benzanilide.....	26	23	—	Terpineol.....	26	30	27
α -Benzaldoxime.....	14	16	18	1, 3, 4, Xylenol.....	17	21	—

respondence the relation (3) is verified for a considerable number of compounds.

TABLE 4
The number of atoms in the molecules of polymerized solids

NAME OF COMPOUND	n KNOWN	n CALCULATED		NAME OF COMPOUND	n KNOWN	n CALCULATED	
		Solid	Liquid			Solid	Liquid
Acetic acid.....	8	16	14	Ethylene cyanide.....	10	21	—
Benzoic acid.....	15	21	19	α Diethylurea.....	20	28	26
α Crotonic acid.....	12	24	24	Phenol.....	13	17	18
Formic acid.....	5	11	9	Hydroquinone.....	14	23	—
+ Trimethylacetic acid..	17	24	23	Quinone.....	12	18	—
Anisic alcohol.....	20	27	23	Resorcinol.....	14	18	—
Acetamide.....	9	18	18	Thiourea.....	8	19	—
Propionamide.....	12	23	—	Trimethylcarbinol.....	15	32	21
Anthraquinone.....	24	31	22	Urea.....	8	18	—
Benzene.....	12	20	15				

TABLE 5
Number of atoms for C = 70

NAME OF COMPOUND	n KNOWN	n CALCULATED		NAME OF COMPOUND	n KNOWN	n CALCULATED	
		Solid	Liquid			Solid	Liquid
Benzoic anhydride.....	27	14	26	Hexadecane.....	50	34	56
Azobenzene.....	24	16	22	Levulose.....	24	11	—
+ Cetyl alcohol.....	51	31	56	Mannitol.....	26	14	—
Benzyl-naphthalene.....	31	16	29	+ Nonadecane.....	59	31	59
Codeine.....	43	21	—	+ Octadecane.....	56	30	56
Ethyl cinnamate.....	25	14	25	+ Octadecylene.....	54	27	56
Diphenylamine.....	24	16	25	s Octadecylene.....	54	27	56
Glucose.....	24	11	—	Picric acid.....	19	10	—

Table 4 includes compounds which show the phenomenon of molecular polymerization in the solid state. Formic acid, acetic acid, acetamide, propamide, ethylene cyanide, urea, etc. appear with double molecules.

Table 5 shows that the values n calculated on the basis of the constant $C = 70$ are much lower than the known values, most of

them being exactly half the first. With the constant $C = 50$, we obtain for n values equal to those of the first column. In this last case, $C = 50$, these compounds are not more polymerized in the solid state than in the liquid state. In changing the value of the constant for these compounds, we must also make $C = 50$ for the compounds in the preceding tables. We must then also modify the conclusions. The fact that these compounds are polymerized in the solid state remains correct, yet the degree of polymerization must be doubled. Formic acid and the other compounds which we mentioned above have molecules four times polymerized in the solid state, that is, twice as much as in the liquid state. It is known that for liquids the degree of polymerization decreases as the temperature is raised. Since it is natural that when the temperature is lowered, polymerization increases it is logical that we should find a greater degree of polymerization in the solid state. The compounds in table 3 present the phenomenon of polymerization, having for the most part double molecules for they tend to polymerize in the liquid state. Molecules of water in the solid state will, in this case, be 10 times polymerized, while they would be only 6 times polymerized with the constant $C = 70$.

The values of the constant C as a function of the atomic weights of constituent elements. For compounds containing bromine, iodine, etc., elements with high atomic weights, the results do not agree. The reason for this difference is the dissimilarity of the respective atomic weights.

In fact, the compounds C_2H_5Cl , C_2H_5Br , and C_2H_5I always contain the same number of atoms, but the mass of the atom chlorine, bromine and iodine is not in the same ration with respect to the mass of the other atoms. The mass of the atom of bromine is almost 3 times and that of the atom of iodine is 4 times the mass of the other seven atoms taken together. To obtain concordant results in this last case, it is sufficient to give to the constant a value which is a function of the atomic weights of the constituent elements. The determination of these values is very easy for organic compounds of bromine, iodine and some other elements.

TABLE 6
The number of atoms for halides, with C corrected

NAME OF COMPOUND	TEMPERATURE OF		DENSITY	% CALCULATED		% KNOWN
	Fusion	Boiling		Solid	Liquid	
Ethyl bromide.....	—	428	1.52	—	12	12
Propyl bromide.....	—	456	1.4	—	17	15
Allyl bromide.....	—	493	1.57	—	15	14
Amyl bromide.....	—	311	1.47	—	7	8
Monobromobenzene.....	—	402	1.25	—	16	17
Benzoyl bromide	—	344	1.38	—	10	11
Monobromotoluene....	—	343	1.46	—	9	9
α monobromonaphthalene.....	—	550	1.5	—	21	18
Phosphorus bromide	—	448	2.93	—	4	4
Phosphorus oxybromide.....	319	468	2.82	10	6	5
Phosphorus thiobromide....	311	—	2.85	10	—	5
Hydrobromic acid ...	—	204	1.78	—	2	2
Boron bromide.....	—	364	2.69	—	3	4
Sulfur bromide.....	—	473	2.63	—	5	6
Silicobromoform.....	—	390	2.7	—	4	5
Methyl iodide ...	—	317	2.2	—	5	5
Ethyl iodide.....	—	346	1.98	—	7	8
Propyl iodide	—	376	1.78	—	10	11
Amyl iodide.....	—	428	1.54	—	17	17
Hexyl iodide.....	—	450	1.47	—	21	20
Heptyl iodide ..	—	477	1.40	—	25	23
Octyl iodide.....	—	499	1.35	—	31	26
Acetyl iodide.....	—	381	1.98	—	8	7
Phenyl iodide	—	468	1.83	—	15	12
Hydriodic acid ..	—	239	2.27	—	2	2
Iodine chloride ...	298	—	3.2	12	—	2
Iodic acid.....	443	—	4.63	12	—	5
Potassium iodide.....	896	—	3.06	108	—	2
Potassium iodate.....	833	—	3.98	57	—	5
Silicoiodoform.....	—	439	3.4	—	5	5
Lead ethyl	—	383	2.03	—	18	17
Mercury ethyl.....	—	432	2.44	—	15	15
Mercury methyl.....	—	369	3.07	—	7	9
Tetraethylstannane.....	—	454	1.19	—	31	29
Tetramethylstannane	—	351	1.31	—	15	15
Triethylstannane	—	533	1.41	—	22	22
Antimony ethyl.....	—	431	1.3	—	23	22
Trimethylbismuthine.....	—	385	2.3	—	15	13
Triethylarsine.....	—	413	1.15	—	20	22
Zinc ethyl.....	—	391	1.18	—	18	15

TABLE 6—*Concluded*

NAME OF COMPOUND	TEMPERATURE OF		DENSITY	% CALCULATED		% KNOWN
	Fusion	Boiling		Solid	Liquid	
Zinc methyl.....	—	319	1.39	—	8	9
Antimony chloride.....	344	503	3.06	15	6	4
Antimony bromide.....	363	556	4.15	9	4	4
Silver fluoride.....	708	—	5.8	7	—	2
Silver chloride.....	533	—	5.5	10	—	2
Silver bromide.....	693	—	6.4	14	—	1
Silver iodide.....	813	—	5.6	27	—	2
Silver chlorate.....	503	—	4.4	14	—	5
Silver nitrate.....	471	—	4.35	12	—	5
Arsenic chloride.....	—	407	2.21	—	5	4
Arsenic bromide.....	298	—	3.66	5	—	4
Cobalt chloride (6H ₂ O).....	360	—	1.84	24	—	3 or 21
Chromyl chloride.....	—	389	1.96	—	5	5
Chromic anhydride.....	453	—	2.8	—	16	4
Cuprous chloride.....	683	—	3.7	22	—	2
Cuprous bromide.....	777	—	4.7	18	—	2
Cadmium chloride.....	814	1,179	3.63	53	21	3
Cadmium bromide.....	844	1,079	4.8	32	10	3
Cadmium iodide.....	677	—	4.6	22	—	3
Cadmium nitrate (4H ₂ O).....	453	—	2.9	26	—	9 or 21
Ferric nitrate (18H ₂ O).....	320	—	1.68	23	—	26
Germanium chloride.....	—	359	1.89	—	6	5
Manganous chloride (4H ₂ O).....	361	—	1.56	34	—	3 or 15
Nickel carbonyl.....	—	316	1.84	—	8	9
Lead chloride.....	758	2,173	5.8	90	72	3
Lead tetrachloride.....	258	378	3.18	33	8	5
Lead iodide.....	656	1,173	6.07	60	19	3
Selenium oxychloride.....	283	453	2.44	10	6	4
Stannous chloride.....	523	879	2.7	31	22	3
Stannic chloride.....	—	593	2.3	—	14	5

In fact, these elements produce numerous organic compounds whose densities and boiling points are very well known. By introducing these data into the preceding formula, it is easy to obtain the respective values for the constant. This was the way in which we found the values 79 for bromine, 66 for iodine, and 46 for mercury (7).

Table 6 contains a number of examples showing the evident

agreement of the results obtained. The constants of other elements can be determined with the aid of the following equation:

$$C_{\text{liquid}} = 100 - \frac{A}{3.7} \quad \text{and} \quad C_{\text{solid}} = 50 - \frac{A}{5.7},$$

in which A signifies the atomic weight of the respective elements.

These formulas have a double importance. First, they permit us to generalize our relation and to find valuable indications on the molecular constitution of a great number of organic compounds. In addition, these formulas prove to us that the atomic weight also must be taken into account in our fundamental relation.

We finally arrive at this important conclusion that the known quantities for our relation are: melting or boiling point of a compound, its density (which represents its molecular weight and the number of molecules in a unit volume), the number of atoms, and the weight of these atoms.

This formula for the liquid state can therefore be written in the form:

$$A = 3.7 \left[100 - \frac{T}{D n} \right] \quad (4)$$

which gives for lead ethyl, mercury ethyl, ethyl bromide, ethyl iodide, tetramethyl stannane, bismuth trimethyl and antimony ethyl values 196; 203; 133; 76; 122; 199; 111 close to the atomic weights of lead 206, of mercury 200, of iodine 127, of bromine 80, of tin 118, of bismuth 208 and of antimony 120. The conclusion drawn from these examples is that organic compounds, which contain an element with a high atomic weight are governed by this atomic weight.

The value of the constant C for different pressures of boiling. We have used above the boiling points of compounds at normal pressure, 760 mm. It is necessary, as Ph. A. Guye showed in 1903, to determine the numerical values of the constant for lower pressures in order to calculate n for compounds which boil only

under vacuum. This determination does not present any difficulty. The relation (2) can be written in the form:

$$T_{760} = 100 \times D \sqrt{n};$$

$$T_p = C_p \times D \sqrt{n}$$

whence

$$C_p = 100 \frac{T_p}{T_{760}}$$

The question is reduced then to a calculation of the ratio of the temperatures of boiling under pressure p and at normal pressure. The calculation of n thus becomes possible even for pressures lower than normal (8).

THE DEGREE OF ASSOCIATION OF INORGANIC COMPOUNDS IN THE LIQUID AND THE SOLID STATE

For inorganic compounds, the degree of association can be calculated with the same exactness as for organic compounds. The melting and boiling points of oxides, acids, salts, bases and elements are much higher than those of organic compounds. We found, as did Vernon, that hydrofluoric acid is four times polymerized. Liquid sulfur has the molecule S_{12} . Oxides of chlorine and of nitrogen, phosphorus trichloride, and the halogen compounds of carbon and of silicon are normal, as found by Ramsay and Traube. Nitric acid we found normal, while it is doubly polymerized according to Vernon and Ramsay. Sulfuric acid, normal according to us, would be four times polymerized according to Vernon but only twice according to Vaubel. Carbon disulfide is doubly polymerized according to Vaubel and us. Sulfur dioxide, normal according to Vernon and us, would be twice polymerized according to Vaubel. Phosphorus would have, according to us, nine atoms in the liquid molecule, while according to Vaubel and Ramsay, it would have only four (9),

The degree of association for elements and salts in the solid state is entirely unexpected and large. Thus carbon, silicon,

lithium, and calcium have a degree of polymerization greater than 200. Beryllium, magnesium, and strontium have more than 100 atoms in a molecule in the solid state. For sodium, aluminum, and potassium the number of atoms in a molecule is greater than 50. Chromium, manganese, iron, cobalt and nickel are polymerized without their degree of polymerization exceeding thirty.

This enormous polymerization of metals, given by our method, is in marked opposition to the idea generally accepted that metals are monoatomic even in the solid state. This is the reason we believe that the constant C must have values much greater than 100 and 50 respectively for compounds whose melting and boiling points are greater than 800°.

On the other hand the value of the constant is less than 100 for liquefied gases such as He (23.8) Ne (16) Ar (44.1) O (56.3) and N (67.8) considering the molecules of these elements as diatomic in the liquid state. As an exception, liquid hydrogen has the constant $C = 208$, which signifies that liquid hydrogen is strongly polymerized (10).

THE SECOND METHOD OF G. G. LONGINESCU

We established, in 1908, (11) the relation:

$$\frac{T}{M} \frac{1000}{T} = 64,$$

in which T signifies the boiling point and M the molecular weight of the compound. This relation provided us with the simplest and surest method for differentiating between a polymerized and a normal compound. The hydrocarbons, ethers, esters, organic halogens, and organometallic compounds appear absolutely normal, having for the constant a value between 63 and 65. Yet all the polymerized compounds give values greater than 64, reaching a value of 99.2 for water, which appears once more as the most polymerized liquid.

We mention only the values of the constant for the first members of each polymerizing series. Thus, we have for formic acid the value 72, methyl alcohol 76.8, aldehyde 67, methyl amine 69,

nitrile methane 73.4 and nitrobenzene 66.4. Among inorganic compounds we found the following normal in the liquid state: Cl₂ 64.8, Br₂ 64, HCl 63.5, HBr 66.7, SOCl₂ 63.2, SO₂Cl₂ 63.3, Cl₂O 64, NOBr 64.5, PCl₃ 63.3, AsCl₃ 63.2, AsF₃ 63.3, POCl₃ 63.1, PSCl₃ 63.3, S₂Cl₂ 63.6, CrO₂Cl₂ 63.2, SnCl₄ 65.5, SiCl₄ 64.6, GeCl₄ 65.1, GeHCl₃ 64.5, TiCl₄ 63, VCl₄ 63.2, VOCl₃ 63.2, SO₂ 63.2, SO₃ 65.2, SO₃ HCl 65, (CN)₂ 63.4, CS₂ 64.1, H₂S 63.7, Fe (CO)₅ 64, N₂O 63.1, Hg₂ 63.1. Among inorganic compounds polymerized in the liquid state we found water 99.2, HF 78.8, CNH 74.8, NH₃ 75.8, NO 67.4, N₂H₄ 83.4.

It can be seen that this method is superior to the first one indicated above. In fact, it gives exact results for all the elements, it permits a distinct separation of normal from associated compounds, and is unexpectedly sure and simple for inorganic compounds. On the contrary, this method is inferior to the first in determining the degree of association. It shows only whether a compound is more or less associated than another, for example that methyl alcohol 76.8 is more associated than formic acid 72.

Liquified gases, considered as diatomic, give the following values for the constant: He₂ 701.4, Ne₂ 258, Ar₂ 111.7, H₂ 83, N₂ 82, O₂ 78. They then will be polymerized in the liquid state and the rare gases, enormously polymerized.

Because of the fact that this relation is an equation of the second degree, it admits two values for the molecular weights. The result is a strange phenomenon, it is true, but a very important one, namely, that a liquid compound is a molecular complex of polymerized and dissociated molecules.

A GLANCE AT OTHER METHODS

A complete analysis of all the known methods is not needed since we have three substantial works on this problem, those of W. E. S. Turner, *Molecular Association*, London, 1915; of P. Walden, *Molekulargrößen von Elektrolyten in Nicht-wasserigen Lünsgsmitteln*, Leipzig, 1923; and of S. Smiles, *The Relations between Chemical Constitution and some Physical Properties*, Longmans, Green and Co. (1910). Among the well established methods are those of Ramsay and Shields, Morgan, Bratschinski,

Mitchell and Bennett, Walden, Bingham, Traube, Guye, and Holmes. These methods are not only complicated but inexact in their results.

Vaubel (12) determines the molecular weight in the solid state by the use of new relations between the osmotic pressure, the lowering of the freezing point and the elevation of the boiling point in equimolecular solutions. Jorissen uses the formula

$$n = \frac{193 M^2}{T_b d_b}$$

where d_b represents the density at the boiling point and T the boiling temperature, the formula being verified for forty substances. W. Herz (13) established the relation

$$\frac{M_k}{d_k} = \frac{M_b}{d_b} = \text{a constant}$$

where M is the molecular weight and d the density, while k and e refer to the critical temperature and the boiling point respectively. This ratio must be unity for normal compounds but not for associated compounds. He also established the relation

$$\frac{M_k}{M_b} = 2.69 \frac{d_k}{d_b}$$

This ratio has a value of 0.98 for esters, 0.97 for methyl, ethyl and propyl alcohols, and 0.99 for acetic acid.

Ph.A. Guye (14) has criticized methods of determining molecular size as follows:

All formulas using as experimental data the surface tension, i.e., a property of the surface layer separating the liquid phase from the vapor phase (including those of Ramsay and Shields, Ramsay and Ross Innes, Kistiakowski, Walden, Dutoit and others) cannot give an indication of the molecular complexity except in this surface film. This complexity is doubtless very often the same as in the mass of liquid, but it is not always and necessarily so.

Neither can certain other relations, apparently independent of surface tension, be accepted as really giving the molecular size in the

liquid phase. These are those which are a function of the boiling point (or what amounts to the same thing, the critical temperature) such as, for example, Trouton's relation and Longinescu's formula. It is easy to demonstrate that relations of this class give a value for molecular size which must generally lie between that which characterizes the inner liquid mass and that of the surface layer.

In fact, the boiling point is that at which, under a pressure of one atmosphere, the number of molecules passing through the surface layer in both directions, i.e., from the liquid phase to the vapor phase and vice versa, is strictly the same in unit time. Now it is clear, that if the surface layer is polymerized in comparison with the liquid mass, the boiling point thus defined will be raised above its normal value. If this layer is partially dissociated, this temperature will be lowered.

Consequently, in the case of Trouton's formula, for example, the denominator T will be too large if the surface layer is polymerized. On the other hand, in the numerator the term λ will include not only the heat of physical vaporization, but also the heat of chemical depolymerization of associated molecules. According to the relative import of these two terms, it will be possible to produce a sort of compensation which explains why in certain cases, with nitriles for example, the Trouton formula indicates as normal, liquids that are clearly polymerized in the surface layer. This almost amounts to saying that when a liquid has not the same complexity in the surface layer as in the inner liquid mass, the use of Trouton's formula is no longer possible.

As for Longinescu's formula, one of his terms, T , depends on the surface layer, the other, d , depends on the liquid mass and is independent of the surface layer. If there is polymerization in the surface layer, T will be too large and consequently n (or, what amounts to the same, the molecular weight) will be too large also. If there is dissociation in the surface layer, T will be too small and also n . Consequently, the Longinescu formula will give results of the same kind as formulas based on surface tension, with this difference, however, that the degree of association or dissociation indicated by this relation will be generally intermediate between that which exists in the surface layer and that in the mass of the liquid. This is generally known to be so.

The most rational physical properties to use in the exact determination of the molecular size in the liquid phase must be completely independent of the properties of the surface layer. In this case, then, it is necessary to exclude surface tension, boiling point, vapor tension, and latent heat of vaporization. These constants can lead only to approxi-

mate results which must be considered only as indications and not as determinations, especially when they are abnormal. Among the properties of liquids, on which research must be carried to obtain exact values for molecular weight in the liquid phase there may be mentioned density, coefficients of expansion and compressibility and viscosity as leading to most reliable conclusions. In this direction some very interesting experiments have already been done by Traube, Walden, Duclau and others.

RECENT WORK ON MOLECULAR ASSOCIATION

It is beyond our scope to analyze in detail the large amount of work on this subject published up to the present. We shall, however, summarize the work which has appeared since 1922.

Frederick G. Keyes (15) calculates the association of CO_2 from the Joule-Thomson effect. He finds that for -53° , there is one double molecule of CO_2 for 500 simple molecules and at 127° one double molecule for 20,000 simple molecules.

E. E. Walker (16) studies the molecular association of compressed gases and proves that only substances the molecules of which are of the same length are truly corresponding substances. For associated compounds an associated factor must be introduced into the critical constants.

N. Vasilescu Karpen (17) establishes a new relation for the calculation of internal pressure of liquids and a criterion for molecular association. He calculates the total work produced by isothermal expansion from the increase in volume, the mechanical equivalent of heat, the heat absorbed and the latent heat of expansion. Deviations prove a molecular association.

J. A. Müller (18) calculates the degree of polymerization at the critical point,

$$x = \frac{3}{8} \frac{RT_c}{P_c V_c}$$

He shows that all except helium, having $x = 0.923$, are polymerized. For normal gases, x is very slightly raised, $\text{H} = 1.22$, $\text{O} = 1.283$, $\text{N} = 1.285$, $\text{A} = 1.285$, $\text{Cl} = 1.363$. Hydrocarbons

have $x = 1.4$, ethers the same, ethyl alcohol 1.5, acetic acid 1.8, acetonitrile 2, and water 1.84.

A. Leduc (19) calculates the degree of polymerization from the equation of state for CO_2 as four percent in saturated vapors.

Carl Wagner (20) uses Trouton's rule as a criterion for association. Among other values, he finds water 26, ethyl alcohol 27.1 and propyl alcohol 26.9.

K. Stachorskii (21) calculates the degree of association at the boiling point with the aid of the molecular weight, the boiling point, surface tension and specific volume.

Luise Lange (22) studies the relation between the dielectric constant and the degree of association of liquids. According to Debye's theory the polar moment is influenced by association. The author finds the following polar moments, multiplied by 10^{-18} , nitrobenzene 3.84, pyridine 2.11, ether 1.22, propyl alcohol 1.53, butyl alcohol 1.65, isobutyl alcohol 1.75, and iso-amyl alcohol 1.76.

M. F. Carrol (23) starts with the hypothesis that association is a general property of all substances, normal ones included. He modifies the equation of state by replacing the constants a and b of Van der Waal's equation by the functions of the degree of association. According to his experiments, the heat of association increases with temperature for associated substances, while it is constant for normal ones.

Louis Harris (24) deduces from the absorption spectrum of vapors, that formic acid has simple molecules at room temperature. On increasing the temperature, the associated molecules become more numerous.

F. Schuster (25) establishes a relation between internal pressure and the covolume and determines the degree of association of a molecular volume, by a modification of Traube's method. He obtains values at the boiling point agreeing with values found by other methods.

C. P. Zahn (26) studies the variation of the dielectric constant of water vapor with pressure and temperature. By interpreting results obtained with the aid of Debye's formula, he explains the anomaly observed at 47° by the formation of an absorption layer

on the condenser plates and not by molecular association as has been proposed by Jona.

D. B. MacLeod (27) establishes a linear relation which shows that the viscosity of a liquid is proportional to the molecular weight, the degree of association and the space unoccupied by molecules. The degree of association can be calculated at any temperature, if it is known at one temperature.

G. Bredig and L. Teichmann (28) established the degree of association for hydrocyanic acid as 2.04, deduced from newly determined critical constants.

Kwantaro Endo (29) determines from the distribution coefficient that phenol in benzene is in great part tripolymerized and with the aid of cryoscopy, that phenol in water is similarly tripolymerized.

Frederick Stanley Brown and Charles R. Bury (30) in determinations by cryoscopic methods with solvents dried by phosphorus pentoxide or partially saturated with water, find that alcohols and phenols are more associated in wet solvents and that their degree of association increases with concentration, while organic acids are more associated in dry solvents.

Jacques Duclaux (31) considers water, according to Röntgen's hypothesis, as an ice solution, containing polymerized molecules identical with those present in ice and accordingly lighter than water. With Sutherland, he calls hydrol "that which remains when the dissolved ice is removed from the real water; real water is a solution of ice in hydrol." The conclusions of Duclaux are as follows:

The study of the variation in the coefficient of expansion of water with pressure leads to the assigning of a formula intermediate between $(\text{H}_2\text{O})_9$ and $(\text{H}_2\text{O})_{12}$ to the molecules of ice.

The study of the variation of compressibility with temperature shows that the relative change per degree of the quantity of ice dissolved in water at 0° is greater than 0.02. . . . The heat of depolymerization of a molecule of dissolved ice is greater than 3000 calories. . . . The heating of water produces both the expansion of the non-polymerized part and the melting of a part of the ice, whence a contraction results, which decreases the coefficient of expansion of water.

The following values are the most probable: The molecule of ice is $(H_2O)_9$ or $(H_2O)_{12}$. The heat of depolymerization of a molecule of dissolved ice is about 4000 calories. A liter of water contains at 0° about 200 g. of ice. In the neighborhood of 0° , this quantity diminishes about 4 g. per degree. The specific heat of dissolved ice is 0.62, that of non-polymerized water 0.99.

The compressibility of depolymerized water at 0° is about 360×10^{-7} and increases about $\frac{1}{810}$ per degree. Pressure diminishes the quantity of dissolved ice by about 0.14 g. per atmosphere. Under a pressure of 3000 atmospheres water contains only about 10 g. of ice. . . . It should be said that most of the methods assume that the molecules of non-associated normal liquids are simple. This hypothesis is perhaps not necessary since the disagreement would disappear entirely if normal liquids were formed of double and triple molecules.

G. Tammann (32) studied the molecular complexity of water in detail basing his work on the existence of a type of molecule characterized by large volume and possessing the reticular structure of ice I. At 0° water contains 0.22 molecules of the ice I while at 50° the concentration of it is very small. The other types of molecules of water are not as easy to recognize and distinguish. On the assumption that molecules of the four kinds of ice can also be found in water, there must exist four types of water molecules, polymerized or isomeric with each other. As pressure is increased the molecules of type I diminish in number and at above 2500 kgm. $cm.^2$ ice III crystallizes, heavier than water. The existence of type I is proved by different physical phenomena which vary with pressure and temperature. At high temperatures and low pressures, water contains molecules of $(H_2O)_2$ which were recognized by W. Nernst. As to the other types of molecules and their weights, we know little about them.

Tammann next studied the concentration of molecules of type I at $0^\circ C.$, the relation between type I and others, the change of volume with the transformation of molecules of type I, the degree of polymerization of type I, the heat of transformation of molecules of type I, the variation of specific heat of water with temperature, the influence of molecules of type I on the viscosity of water in relation to pressure and temperature, and the variation

of the surface tension of water with pressure and temperature. The refractive index of ice is greater than that of water, for the number of molecules of type I increases by crystallization. The article closes with the following conclusion: "The determination of the concentration of molecules of type I permits the thermodynamic calculation of their molecular weights, $(\text{H}_2\text{O})_9$ in case these molecules dissociate into 9 H_2O , and $(\text{H}_2\text{O})_4$ in case they dissociate into 2 $(\text{H}_2\text{O})_2$."

G. Antonoff (33) commences his article "Sur la structure moléculaire des liquides et des solides" as follows:

Present ideas on the nature of liquids are somewhat lacking in coordination and in general no one of the recent theories is of a sufficiently comprehensive character to solve the enigma of the liquid state. It has been considered that liquids can be divided into "normal liquids" and "abnormal liquids." The first have been so named because they obey some empirical laws devoid of all theoretical basis. If a phenomenon appears abnormal from the point of view of a law based on a limited number of facts, this signifies that the true law has not been found. This is sufficiently demonstrated with liquids. Researches have resulted based on purely empirical points of view in the minds of most investigators, with an accumulation of detailed facts but without a satisfactory theory or even a fruitful hypothesis. A great amount of work has been done on the study of solutions, i.e., on mixtures of different liquids, and the results is that the problem of liquids, already a difficult one, has been further complicated through the mutual action of two liquids, whose individual nature has not yet been defined. . . . of two liquids, whose individual nature had not yet been defined. . . . In the present state of our knowledge there is no method, direct or indirect, which permits the determination of the molecular weight of liquids . . . , and no theory indicates where and when the phenomenon of association is produced.

Antonoff passes next to the study of solutions and continues:

Van't Hoff has shown that dissolved materials obey the laws of the gaseous state. These laws can be verified for dilute solutions. But in more concentrated solutions appreciable deviations are encountered. As in the case of gases, it is natural to assume that if simple laws are not applicable, this is due to molecular forces which cannot be neglected

at high concentrations where the distance between molecules becomes small and the field of molecular forces distinctly appreciable. I have, nevertheless, reason to believe that molecular forces have no effect on the above properties.

Antonoff's conclusions are:

The fact that at the critical point separation occurs into two phases of equal volume, indicates that one-third of the molecules attach themselves to another third to form double molecules. Thus at the critical point, the system will contain an equal number of double and simple molecules, which after separation occupy equal volumes. The different phases in equilibrium with each other contain the same number of molecules per unit volume.

In his article, "Propriétés physiques des liquides fonctions de la température" (34) Antonoff establishes the fact that the properties of liquids vary discontinuously as a function of temperature. The discontinuities are distinctly greater than the experimental error. He concludes that the facts are perfectly explained by the hypothesis that matter is subject to molecular changes such that at relatively low temperatures only very complex aggregates of molecules are present as elementary constituents.

H. Brereton Baker (35) studied the change of properties of substances under prolonged drying during years or even decades. We propose the term ultra-drying for this kind of drying. Entirely unexpected changes in properties were found under this treatment. The boiling points of ten liquids ultra-dried with P_2O_5 show a considerable rise. The melting points of sulfur and iodine show rises of 5.5° and 2° respectively after nine years of ultra-drying. The melting points of sulfur trioxide ultra-dried for twenty years and of bromine and benzene so dried for ten years were found to be 61° , -45° , 6° respectively. The vapor density of ether, ultra-dried for ten years, was found to be 81.7, twice the normal value, and that of methyl alcohol, ultra-dried also for ten years, to be 45, while the normal is 15. Baker explains these transformations by the polymerization of the respective molecules after the removal of water. Even benzene and hexane, considered as normal hydrocarbons, appear to be asso-

ciated. In an ordinary liquid, there would be a continual combination and separation of molecules.

In other experiments, Baker (36) used catalysts, wood charcoal, platinum black, or thorium oxide, and measured the vapor pressure and surface tension, before and after the action of the catalyst. In general, vapor pressure was found to be greater in the presence of the catalyst. The longer the time of contact with the catalyst, the greater was the molecular weight found to be. Thus acetic acid, after a day's contact with wood charcoal, had a molecular weight of 1.5×60 , after three weeks 2.5×60 , and after 12 months 2.49×60 . In contact with platinum black it had a molecular weight of 2.4×60 after two weeks and of 2.97×60 after eight months. Water in contact with platinum had a molecular weight of 3.352×18 on the first day and of 4.442×18 after six months. Slightly lower values were obtained with thorium oxide.

According to Baker liquids can be compared to dissociable gases such as N_2O_4 . At low temperatures the heavy molecules predominate, at higher temperatures light ones. Association, like dissociation of molecules, takes place much more slowly for liquids than for gases. In liquids, the equilibrium can be easily disturbed by even a slight change of temperature and the return to normal conditions takes a long time, sometimes even months. In the same way the effect of the catalyst is produced much more slowly in a liquid than in a gas.

Roland Herbert Purcell (37) studied the action of ultra-drying on certain chemical reactions. Thus the reduction of copper oxide by carbon monoxide without drying takes place in 90 minutes at 100° , and after a drying of ten days in twenty hours. In the same way, Bi_2O_3 is reduced by CO without drying in a few minutes at 250° and after ten weeks drying, the reduction is produced only at 450° . On the other hand, HgO is easily reduced by CO at 180° , even after a drying of eight months.

The Earl of Berkeley (38) proposes an experimental method for the investigation of molecular association which is based on an optical measurement of the density of the various portions of a liquid confined in a centrifuge tube which can be rotated at a

velocity which may prove sufficient to separate the constituents of a liquid into fractions of different densities. If this proves feasible valuable information can be obtained. While the proposal includes the separation of isotopes by this method, several million times the force of gravity would have to be attained, for Svedberg's latest model of the ultra-centrifuge, which multiplies gravity by 42,000 has effected separations of molecular types only when the difference in molecular weight was some ten thousand fold.

THE NEW THEORY OF MOLAR CONCENTRATION OF G. G. LONGINESCU
AND GABRIELA CHABORSKI

The present state of knowledge of molecular association is, as has been shown, entirely chaotic. The idea of molecular association has not even led to concordant results. In fact, the degree of association determined for the same compound very often differs greatly from one method to another. On the other hand, since the degree of association is never an integer, there are present some simple molecules as well as associated ones, i.e., double, triple, and even more complex ones. This lack of homogeneity in the constitution of the liquids as well as in the results obtained fails to give sufficient basis for a good theory. It is necessary to abandon the paths followed in the past. The idea of molar concentration has opened a new and promising approach.

Dr. Gabriela Chaborski has expressed the opinion that the phenomenon of molecular association, or more exactly the phenomena which distinguish associated liquids from normal ones, are not due to simple molecular association, but to the accumulation or crowding of the molecules into a given volume of pure compound Molecular association is reduced, according to her, to a question of concentration of gram molecules in a given volume. This new conception has been very fruitful in its results.

The molar concentration C_m , of a pure liquid or solid is the number of gram-molecules contained in a liter of the solid or liquid compound and is given by the expression:

$$C_m = \frac{1000d}{m}$$

Thus the molar concentration of ether, whose density is 0.714 and molecular weight 74.08, is 9.6, which means that in a liter of pure ether there are 9.6 gram-molecules of ether. Similarly the molar concentration of carbon tetrachloride is 10.4, that of toluene 9.4, that of benzene 11.2, and that of water, the largest of all, 55.5.

For 350 compounds studied by us the values for the molar concentration all lie between 55.5 for water and 0.09 for tristearin.

TABLE 7
Comparison of molecular association with molar concentration

SUBSTANCE	DEGREE OF ASSOCIATION X	$\frac{C_m}{10} = 100 \frac{d}{m}$ (Longinescu-Chaboraki)
1. Toluene.....	0.94 (Ramsay-Shields)	0.94
2. Carbon tetrachloride	1.01 (Ramsay-Shields)	1.04
3. Monochlorobenzene	0.99 (Walden)	0.98
4. Monobromobenzene.....	0.94 (Longinescu)	0.95
5. Ethyl alcohol.	1.8 (Walden; Bingham)	1.71
6. Phenol.....	1.13 (Walden)	1.13
7. Propanol.....	1.4 (Longinescu)	1.39
8. Chloral.....	1.02 (Ramsay-Shields)	1.02
9. Acetic acid	1.75 (Longinescu)	1.75
10. Acetic anhydride	1.04 (Ramsay-Shields)	1.06
11. Nitroethane.....	1.40 (Longinescu)	1.39
12. Aniline	1.05 (Ramsay-Shields)	1.10
13. Benzonitrile.	0.97 (Ramsay-Shields)	0.97
14. Ethyl ether.....	0.99 (Ramsay-Shields)	0.99
15. Methyl formate.....	1.62 (Traube)	1.60
16. Ethyl acetate	1.08 (Walden)	1.05

All organic liquids which are considered associated have a molar concentration greater than 10. For normal liquids, whose degree of association x approaches 1, the molar concentration is 10 or very close to 10. Therefore, for all liquids, the degree of association is equal to a tenth of the molar concentration, that is:

$$x = \frac{100d}{m}$$

In many cases, the agreement between the degree of molecular accumulation and the degree of molecular association is perfect, as is shown in table 7. This indicates that molar concentration

is the common point of contact of the various physical constants with the help of which the degree of association has been determined.

For instance the lowering of the freezing point of liquids gives values which are often either larger or smaller than those which correspond to the simple molecule. When Δ is found to be smaller, the variation is explained on the hypothesis of molecular association, i.e., by a molecular weight greater than that of the gaseous state. When, on the contrary, values found for Δ are larger than they should be, the explanation is found in the hypothesis of a non-electrolytic dissociation.

The values of Δ would no longer appear as abnormal and all the discrepancies are easily explained, if Δ is expressed as:

$$\Delta = C \frac{g}{MG}$$

i.e., as a function of molar concentration. The degree of association x is expressed by the ratio between molecular weight M' calculated from cryoscopic data and the simple molecular weight:

$$\frac{M'}{M} = x.$$

on the other hand, the degree of association is approximately equal to a tenth of the molar concentration.

$$\frac{C_m}{10} = x,$$

from which we obtain:

$$\frac{M'}{M} = \frac{C_m}{10} \quad \text{or} \quad M' = M \frac{C_m}{10}$$

By introducing this value of M' into the formula which gives Δ we have:

$$\Delta = C \frac{g}{M \frac{C_m}{10} G},$$

a relation which shows that Δ is inversely proportional to the molar concentration.

All the exceptions, where Δ is larger or smaller than that which corresponds to the simple molecule, are easily and directly explained, without the need of resorting to two contrary hypotheses, that of molecular association and especially that of non-electrolytic dissociation. According to this point of view all these differences are due exclusively to the molar concentration of the substance considered. For instance, in cases where Δ is smaller than the normal value, it is usually assumed that the difference is due to association, which implies an increase of molecular weight and therefore a decrease in the number of free particles. The formula above shows, on the contrary, that the molecular weight remains normal, but that the number of free particles is increased.

The interpretation on the basis of molar concentration has the advantage of employing only a single concept. In the case of liquids for which

$$x = \frac{100d}{m} = \frac{C_m}{10} = \text{approximately } 1,$$

Δ will have a normal value. In the case of compounds for which $x = \frac{C_m}{10}$ is larger than 1, Δ will have a smaller value than normal.

Finally if $x = \frac{C_m}{10}$ is smaller than 1, Δ will have a larger value than normal. This last case is that of substances for which a non-electrolytic dissociation is timidly assumed.

It should be noted that recently the existence of agglomerations of molecules in certain liquids has been ascertained by Röntgen-spectrography. If this is confirmed it will contribute experimental proof of these accumulations in liquids with high molar concentration.

The same simple and single interpretation can be applied to all the exceptional cases of capillary rise. Ramsay and Shields have accepted a temperature coefficient $K = 2.12$ for normal liquids. For associated liquids K is smaller than 2.12 and for those which are supposedly dissociated K is larger than 2.12 and attains a value of 6.21 for tristearin, as determined by P. Walden. Gabriela Chaborski (39) has modified the formula of Ramsay and Shields

by replacing the molecular volumes by their values in molar concentrations:

$$\frac{\gamma_1 \left(\frac{1000}{C_m} \right)^{\frac{1}{2}} \gamma_2 \left(\frac{1000}{C_m} \right)^{\frac{1}{2}}}{t_2 - t_1} = K.$$

This formula shows that all compounds with high molar concentration have a small temperature coefficient. Those with small molar concentration have a large temperature coefficient. There is a satisfactory parallelism between the values of K and those of molar concentration. The agreement goes as far as the value of $K = 6.21$ (tristearin) for which Walden calculated $x = 0.200$ and of which the molar concentration is 0.9.

As for special case of compounds having a degree of association smaller than 1, it seems to us that the idea of molar concentration shows clearly the insufficiency and lack of generality of the idea of molecular association, which has not succeeded in giving a satisfactory explanation of these deviations from the normal value of K . In fact, it can hardly be assumed that these substances undergo a non-electrolytic dissociation, and especially to a degree as high as would be required for tristearin, when we are dealing with pure and stable compounds which can largely be distilled without decomposition at atmospheric pressure. The idea of molar concentration, on the other hand, explains these special cases easily and without any constraint, replacing molecular association by an accumulation of simple molecules and the non-electrolytic dissociation by a depletion of simple molecules.

A NEW EXPRESSION OF AVOGADRO'S LAW

Under the concept of molar concentration there is no molecular complexity; only the number of simple molecules in unit volume varies from one compound to another. When this number exceeds a certain value the phenomenon of molecular accumulation appears. The degree of accumulation is a tenth part of molar concentration and is expressed by $x = \frac{100d}{m}$. All liquids for which the product $100d$ is greater than the molecular weight

in the gaseous state, are polymerized. It is the simplest way of separating associated compounds from non-associated ones. Molar concentration, in its turn, is caused by molecular attraction. Associated liquids, therefore, are compounds in the interior of which the molecular attraction is greater than in non-associated liquids. Associated liquids are really comparable to compressed gases, in which the diminution of volume is greater than that which corresponds to the outside pressure. In the same way that Van der Waals explained the difference in compressibility of gases by molecular attraction we wish to explain molecular association by the internal compression of molecules. Liquids with large molar concentrations are compounds subject to a large internal pressure. We thus achieve a new expression for Avogadro's law. *Equal volumes of fluids, and possibly of solids, at the same temperature and under the same external pressure, contain numbers of simple molecules proportional to the internal pressure.* Associated compounds, non-associated ones, and those considered as dissociated are compounds in which the internal pressure varies from one end of the scale of internal pressures to the other. There must be a proportionality between degrees of molecular accumulation and internal pressures of the respective compounds. This new expression of Avogadro's law is applicable to both the gaseous and the liquid state. Instead of considering acetic acid, water and other compounds as associated in the vapor state, it is simpler to assume that they contain different numbers of molecules in equal volumes. Instead of explaining differences in compressibility of vapors by the formation of associated molecules, it is more natural to attribute these differences to internal attraction and to consider the molecules as remaining simple and non-associated.

Instead of generalizing Avogadro's law, we transform it completely. Instead of modifying the nature of the molecules by their association, we modify their number in unit volume, while preserving their simplicity.

The degree of molecular accumulation comes to the support of these conceptions. In fact, we have $100d = mx$, an analogous expression to $28.9d = m$, which gives the molecular weight in

the gaseous state. This last relation can also be expressed in the general form $28.9d = mx$, applicable to associated compounds like acetic acid in the vapor state. Given that the second relation is the result of Avogadro's law, the first relation, applicable to liquids, is also a result of Avogadro's law. In the same way, the number 28.9 can be considered as the molecular weight of air, the number 100 can be considered as the molecular weight of water in the liquid state by giving the value 5.55 to its degree of molecular association. The molecular weight of a compound in the liquid state is then the product $100d$. On the other hand, as the degree of accumulation is proportional to the molar concentration and as this in turn is proportional to the internal pressure p , it follows that the second relation must take the form:

$$100d = kpm$$

To verify this result it is necessary to know the exact value of the internal pressure p . But that is lacking at present, for the values obtained vary from one method to another just as in the case of the degree of association.

EXPERIMENTS OF I. N. LONGINESCU ON THE INTERNAL PRESSURE OF A FLUID

Based on the works of Amagat, Leduc, Born and especially of Van Laar, I. N. Longinescu (40) determined that the totality of molecular forces of a fluid can be represented by the relation:

$$K \frac{m^2}{d^6}$$

In this formula K is a constant, d is the distance between the centers of two gram-molecules, and m a physical quantity called mass attraction, which plays the same rôle as does Newtonian mass in the phenomena of gravitation and as the electric charge in electrostatic forces. For various reasons the repelling forces are neglected but the results are satisfactory without being absolute. The molecules attract each other according to the 5th

power of the distance, as in the formulas of Tyrrer and Boltzmann. The essential property of the mass attraction is that it is additive.

$$m = c_1 + c_2 + c_3 +$$

In reality the atomic constants c_1 , c_2 , c_3 are valence constants and one atom is capable of having several constants depending on the combination involved.

As for associated substances, agreement between calculated values and known values is obtained by assuming a certain increase of the mass attraction for the respective radicals. The degree of association in each organic series diminishes with the number of carbon atoms because the relative effect of the characteristic radical diminishes also. The advantage of the new theory is that it predicts the degree of association solely on the basis of the chemical formula.

By successive transformations the relation:

$$\frac{T_c}{d_c \sqrt{n}} \quad 450 \text{ is established,}$$

which is the formula of G. G. Longinescu at the critical point. This is the first time that this relation has been obtained theoretically.

The expression

$$\frac{T_c}{d_c \sqrt{n}} = \frac{6000 (c_1 + c_2 + c_3 + \dots)^2}{m \sqrt{n}}$$

is also established by I. N. Longinescu and is the most simplified expression of the generalized formula of G. G. Longinescu. According to I. N. Longinescu the degree of accumulation of Longinescu Chaborski is proportional to the critical temperature and inversely proportional to the number of atoms in the molecule. Thus, CH_3OH has a larger degree of accumulation and a smaller number of atoms in the molecule than $\text{C}_2\text{H}_5\text{OH}$.

The work of this young Roumanian scientist is of great importance. By introducing the concept of mass attraction he has shown that molecular association can be explained solely by the

attraction of simple molecules which varies with the fifth power of the distance.

CONCLUSION

We have now come to the end of the trail made by science during the past fifty years. The ideas of Louis Henry enriched science through the addition of a most important chapter, that of molecular association. If the explanation of this phenomenon "so strange in its nature and so important in its generality" is now based on molecular complexity, the phenomenon itself is interesting and Louis Henry deserves much credit for having called attention to it. With the aid of the concept of molar concentration we have shown that the phenomenon of molecular association is in reality only a phenomenon of simple molecular accumulation. Hence the hypotheses of molecular complexity and of non-electrolytic dissociation are both unnecessary. Molar concentration explains logically, directly and simply all the deviations observed in cryoscopic and capillary measurements. Solids and liquids are composed of simple molecules just as gases are. Associated molecules do not exist; only the concentration of simple molecules varies from one substance to another and is much greater for "associated" than for normal compounds. Avogadro's law must receive a new expression: equal volumes of fluids and possibly of solids, at the same temperature and under the same external pressure, contain numbers of simple molecules proportional to the internal pressure.

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THE PHYSICO-CHEMISTRY OF CREATINE AND CREATININE

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While a vast amount of work has been done in recent years upon the biological relationship of creatine and creatinine,¹ the facts of a purely chemical nature have remained isolated in a number of widely scattered references, quite often appearing in papers the titles of which would not lead one to expect the contents.

Formerly, the lack of sources for creatine and creatinine precluded an exhaustive study of the chemical relationship of these compounds, but in recent years the discovery of a cheap source of supply of creatine (5), and improved methods for the transformation of creatine into creatinine (6) has led to extensive investigation.

It is the purpose of the present paper to make the facts relating to the chemistry of creatine and creatinine more readily available for the biological chemist, as well as other workers in the field.

OCCURRENCE AND PREPARATION

Creatine was discovered in 1834 by von Chevreul in meat extract (7). It has been found in the muscles of vertebrates in constant amounts (8), in the flesh of many animals (9), in the brain (10), in blood (11), and in urine under certain abnormal pathological conditions (12).

Creatinine occurs normally in urine and was discovered therein

¹ An excellent discussion of the metabolism of creatine and creatinine is given by Benedict and Osterberg (1) and subsequent papers of the same series in which the chemical relationship of the compounds involved are given consideration. Pioneer work in this field was done by Folin (2) and by Klercker (3). A very complete summary of the literature through 1922 with reference to creatine-creatinine metabolism is given by Hunter (4), and later through 1926 (69).

by Liebig (13). It has been found in a number of fluids and tissues for the most part of animal origin; in dogs' urine (11), in certain fish (14), in the muscles of mammalia (15), beef extract (16), crab extract (17) and in soils and grain seed (18).

Creatine may be synthesized from cyanamide and sarcosine. It is usually prepared from meat extractives and its preparation in this manner has reduced the price considerably thus making available quantities sufficient for large scale research.

Creatinine was formerly prepared exclusively from urine (19, 20, 21), a long, tedious and expensive process. It is now prepared from creatine, there being several procedures available. The method of Folin and Dennis (22) involves the heating of solid creatine in an autoclave, while that of Benedict (20) involves the intermediate formation of creatinine zinc chloride and subsequent decomposition of this salt with ammonia. Probably the most satisfactory method for all purposes is that of Edgar and Hinegardner (6) the principle of which depends upon the conversion of creatine into creatinine hydrochloride by treatment with hydrochloric acid and subsequent formation of creatinine from this salt by treatment with ammonia. Advantage is taken of the facts that ammonia will liberate creatinine from its salts; that creatinine is only moderately soluble in cold concentrated ammonia; that ammonium chloride is readily soluble under such conditions, and that ammonia has but little tendency to bring about the conversion of creatinine into creatine. A yield of 85 to 90 per cent may be expected, depending upon the technique. It is quite as well adapted to large as to small scale preparation. The product is quite pure, the actual degree depending upon the purity of the original creatine.

PURIFICATION AND PROPERTIES

Creatine may be purified by recrystallization from water at comparatively high temperatures. It is fairly insoluble in cold water and a good yield is obtained in this manner. Charcoal is employed to absorb foreign coloring matter and the final product is pure white, odorless and finely crystalline. The solid thus prepared contains one molecule of water of crystallization (23).

The purification of creatinine by crystallization presents certain difficulties. If water at a high temperature, or aqueous alcohol, is used as solvent there is always the danger that some creatine may be formed and as it is much less soluble in all ordinary solvents than creatinine, it is almost impossible to effect complete separation by crystallization. Undoubtedly the most satisfactory method is that of Edgar and Hinegardner (6) in which one part by weight of creatinine is dissolved in five parts of water previously heated to 65°C. as rapidly as possible; two volumes of acetone are immediately added and the mixture cooled in ice. After standing several hours the precipitated creatinine is filtered off, washed with acetone and dried. About 65 per cent of the product is recovered.

Creatine crystallizes in hard, colorless, bitter monoclinic prisms which lose their water of crystallization at 100°C., becoming then white and opaque.² It is soluble in 74 parts of water at 18°, becoming more soluble in hot water. It is only slightly soluble in alcohol and insoluble in ether. In aqueous solution its reaction is slightly alkaline (13). Its heat of combustion is 4240 calories per gram (25) and its decomposition temperature is 291 to 291.5°C. (corr.) (24), which is 12 to 15°C. lower than the value given by Mulliken (26).

Creatine upon hydrolysis yields methyl-hydantoic acid, urea, methyl-amino-acetic acid and carbon dioxide (27). It reduces boiling mercuric oxide to metallic mercury and the creatine is oxidized to methyl-guanidine and oxalic acid. Its reducing action is, however, far less marked than that of creatinine. Mercuric nitrate in neutral solution precipitates creatine; it is not precipitated by cadmium chloride or lead acetate. Creatine forms soluble normal salts with the mineral acids (28), and readily soluble double compounds with zinc chloride and cadmium chloride (29).

The homologues of creatine are prepared by the action of cyanamide upon the corresponding amino-acids in the presence

² According to Williams and Lasselle (24) four out of five persons to whom samples of creatine were submitted, pronounced the substance tasteless. Its crystals are characterized as being thin, tabular monoclinic prisms

of ammonia (30). Upon treating creatine with absolute alcohol and dry hydrogen chloride, esterification of the carboxyl group is effected, rather than ring closure. In this manner esters were readily obtained with methyl-, ethyl- and n-butyl alcohol (31).

Creatinine crystallizes in anhydrous monoclinic prisms, soluble in 11.5 parts of water and 100 parts of absolute alcohol at 16°C. It is practically insoluble in ether and acetone. Its heat of combustion is 4986 calories per gram (25) and its decomposition temperature is given as 260° to 270°C.

Creatinine is a weak base being displaced by ammonia from its salts and forming soluble salts with the mineral acids (32). It is a much stronger reducing agent than creatine; mercuric oxide is reduced to metallic mercury, and an alkaline solution of copper hydroxide is reduced by creatinine. It forms an easily soluble crystalline compound with hydrochloric acid, and a number of double salts of which creatinine zinc chloride is a typical member (33). A number of the double compounds of creatinine are quite insoluble; viz., creatinine potassium-, rubidium- and cesium picrates, and are useful in isolating small quantities of creatinine (34). It is precipitated by mercuric nitrate and -chloride solutions (35). A number of the acyl- and alkyl-derivatives of creatinine have been prepared (36).

ANALYTICAL

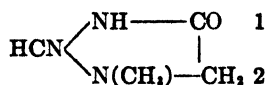
Creatine cannot be estimated quantitatively as such, but is usually converted into creatinine by evaporation with hydrochloric acid and thereby determined.³ Creatinine is almost invariably determined colorimetrically, there being several reactions by which characteristic colorations may be brought about. Weyl's reaction (38) makes use of the addition of a few drops of sodium nitroprusside to an aqueous solution of creatinine in which a ruby-red color develops after making alkaline with sodium hydroxide. Salkowski's reaction (39) is brought about

³ Creatine may be quantitatively converted into creatinine hydrochloride by evaporation with hydrochloric acid to dryness over a steam bath (37), or by passing gaseous hydrogen chloride through creatine solution at room temperature (6). If desired, the creatinine may be displaced by ammonia and hence recovered.

by the addition of excess acetic acid and warming the solution obtained in Weyl's procedure, a distinct yellow coloration being produced.

Jaffe's reaction (40), the development of a red color upon the addition of picric acid⁴ to an aqueous solution of creatinine made alkaline with sodium hydroxide, is almost universally employed for the quantitative estimation of creatinine. The general method as outlined by Folin (42) with later improvements (43) consists in treating 20 cc. of creatinine picrate solution containing 0.5 mgm. creatinine per cubic centimeter (1.5119 grams salt per liter) with 25 cc. saturated picric acid solution and 10 cc. of sodium hydroxide solution (10 per cent). The standard so prepared is allowed to stand for seven minutes and is then compared in a colorimeter with the unknown creatinine solution. Care should be taken to have the two solutions at as nearly equal concentration as possible and treatment of the standard and unknown should be as nearly uniform, in general, as possible.⁵

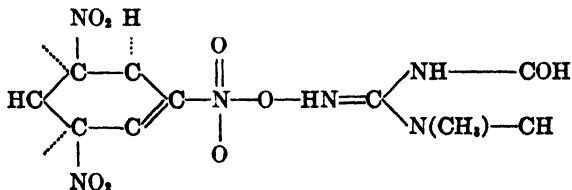
While Jaffe's reaction has been used for some time in the analysis of creatinine, it has been but recently that a study has been made of the chemistry involved (45). Thus it is probable that there is a keto-enol change within the creatinine molecule between positions 1 and 2,



⁴ According to Benedict (41), commercial picric acid is quite unsuited for use in the determination of creatinine *per se*. It was found that many samples yielded a color with alkali alone. For best results the picric acid must be purified. Thus, to 400 grams of commercial picric acid 1 liter of pure benzene is added, heated to boiling and decanted through a filter. Heat the filtrate again in order to bring into solution such picric acid as may have crystallized out, allow to set over night. The crystals are washed twice with benzene and dried in the air. About 85 per cent recovery of acid is obtained.

⁵ According to Morris (44) creatinine may be determined in the presence of acetone, acetoacetic acid or glucose. The creatinine is precipitated as the double salt of potassium and creatinine, the precipitated salt re-dissolved after washing, and the creatinine determined colorimetrically. As standard a solution of potassium creatinine picrate is employed. Precipitation is not complete and a correction factor must be applied.

and a change in the picric acid molecule involving the hydrogens in the meta positions and, probably, all three nitro groups, giving rise to a red tautomer which, for the present, is written



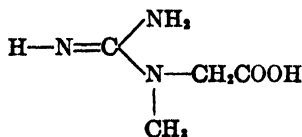
The broken lines indicate that the exact positions of these hydrogens and the disposition of the remaining valencies of the carbon atom are unknown.

According to Chapman (46), the red coloration developed in this reaction is due to the formation of the sodium salts of picramic acid (monoamino-dinitrophenol) and diamino-nitrophenol. Apparently the only foundation for this theory lies in the fact that a match was able to be obtained between the creatinine reaction product and a mixture of these substances.

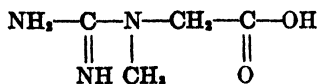
CHEMICAL RELATIONSHIP

While it is not within the scope of this paper to discuss fully the various theories relating to the origin of creatine and creatinine in the processes of metabolism, it is felt that a brief description of some of these would throw much light upon the chemical nature of the two compounds.

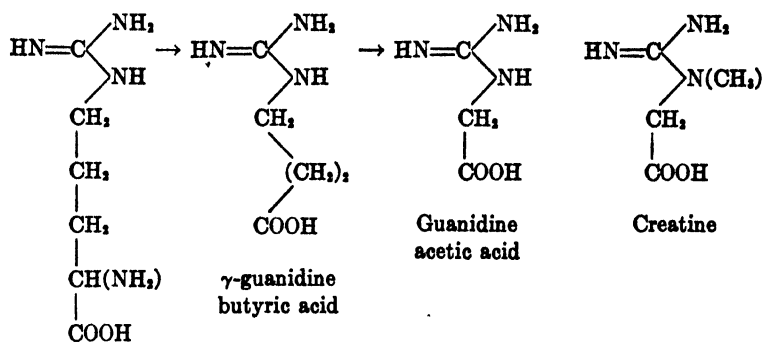
Creatine (Greek *kreas*, flesh) may be considered as methylguanidine-acetic acid,



or as methylglycocyamine,

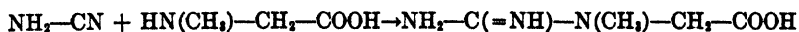


It is thus related to arginine (δ -guanidine- α -amino-valerianic acid), from which it might be derived by methylation:

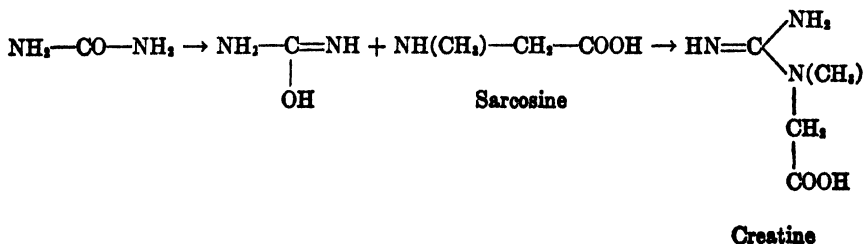


Arginine

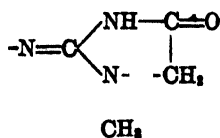
On the other hand, it may be considered as a ureide of methyl glycol, which, with cyanamide, gives creatine. Thus,



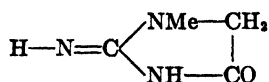
Considering cyanamide as an anhydride urea it may be prepared therefrom by the action of sodium; and cyanamide yields urea when treated with 50 per cent sulfuric acid. It would seem possible according to Mathews (47) that urea might give a similar synthesis with amino-acetic acid. Thus,



Creatinine may be considered as methyl-guanidine-acetic acid anhydride,



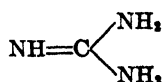
or as l-methylglycocymidine. It may be synthesized by the action of guanidine carbonate,



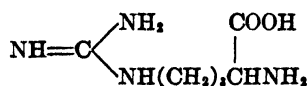
upon sarcosine at 140° to 160°C.

Its discovery as a constituent of soils and vegetable matter seems to point to the fact that it need not necessarily be considered as having origin exclusively in animal matter.

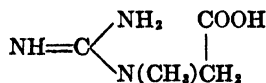
There is a very interesting structural relationship between arginine and guanidine on the one hand, and creatine and creatinine on the other. Thus, according to Shorey (18):



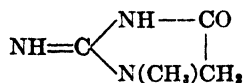
Guanidine



Arginine

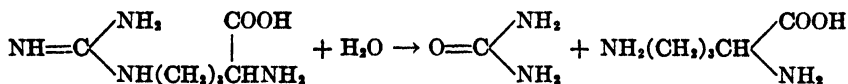


Creatine



Creatinine

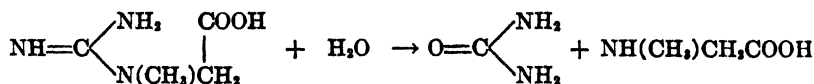
The close relationship existing between arginine and creatine, and thus creatinine, is shown by their behavior upon treatment with barium hydroxide:



Arginine

Urea

Ornithine



Creatine

Urea

Sarcosine

This relationship is also shown in the synthesis of the two compounds, creatine having been synthesized from sarcosine and

cyanamide (48), while that of arginine has been effected by the action of ornithine upon cyanamide (49). As a matter of fact, arginine has been found in the soil (50), and guanidine has been found in plants (51).

The purine bases bear a relationship to guanidine and hence to creatinine, and it is interesting to find that guanine, the only commonly occurring purine base not found in soils, gives guanidine upon oxidation; and further, that guanine is a constituent of organic fertilizers. This possible connection of creatinine with the purine bases and nucleic acids is, however, to be regarded as purely speculative.

PHYSICO-CHEMICAL

From the standpoint of physical chemistry, and perhaps biochemistry as well, the most important property of creatine and creatinine is the readiness with which they are transformed, the one into the other, under the influence of practically every aqueous medium—ammonia solution alone, to which reference has been made, being the only such medium directly inhibiting the mutual transformation. However, a very profound effect upon the extent and direction of the conversion is produced by the nature of the medium. Accordingly, it is necessary to consider the reaction in the light of these effects.

IN AQUEOUS SOLUTION

As early as 1847 Heintz (52) found that a precipitate of creatinine zinc chloride is produced upon cooling a solution of creatine which had been boiled with zinc chloride. Again, Wörner (53) obtained Weyl's reaction for creatinine by merely heating a solution of creatine to the boiling point, and further found that such a solution deposits crystals of creatinine picrate upon treatment with picric acid and allowing to stand. The complete conversion of creatine to creatinine in aqueous solution has been reported by Neubauer (54) when the solution is heated at the boiling point for several days in a closed tube, and the partial conversion by simply evaporating slowly upon the water-bath.

The reverse transformation is not so readily detected although

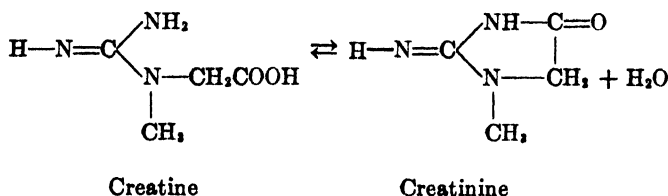
Dessaigues (55) showed in 1857 that creatinine was slowly converted into creatine, more rapidly by heating, under the influence of water alone. Later, Johnson (56) was able to convert creatinine almost completely into creatine by evaporating a solution of the former and removing the crystals of the latter from time to time as they were formed.

These facts, while purely qualitative, nevertheless indicated that the reaction was reversible. Considering the importance of the transformation in the theory of metabolism, it is surprising that the rigorous characterization of the equilibrium conditions

TABLE 1
Equilibrium constants at several temperatures

	25°C.	50°C.	70°C.	100°C.
K.....	0.54	1.02	1.59	2.89

in aqueous solution has but recently been accomplished. Thus in 1925, Edgar and Shiver investigated the reversible reaction (23),



and from the expression,

$$K = \frac{(\text{Creatinine})}{(\text{Creatine})}$$

obtained the results shown in table 1.

The results show conclusively that the reaction proceeds definitely to a condition of equilibrium in aqueous solution; that the equilibrium is markedly affected by temperature; and that the proportion of creatinine is increased with increasing temperature. Obviously, the statement occasionally appearing in the literature

that creatine can be quantitatively converted to creatinine by continued boiling with water alone is incorrect.

From the values of K at the several temperatures employed an equation has been derived from that of van't Hoff (the reaction isochore)

$$\frac{d \ln K}{d T} = \frac{\Delta H}{RT^2}$$

for calculating the equilibrium constant at any temperature. Solution of the above yields for ΔH , the heat absorbed in the reaction, the value 4963 calories. Integrating and converting to ordinary logarithms, this expression becomes

$$\log K = \frac{-\Delta H}{2.303 T} + C$$

and by substitution of the appropriate values of ΔH , K and T , the mean value of C , the constant of integration, becomes 3.3652.

TABLE 2
Comparison of results

	25°C.	50°C.	70°C.	100°C.
K , calculated.....	0.541	1.024	1.604	2.830
K , determined.....	0.540	1.022	1.593	2.890

Thus the value of the equilibrium constant at any temperature may be calculated by the expression,

$$\log K = \frac{-1084}{T} + 3.3652$$

In table 2 is given a comparison of the results experimentally determined with those calculated from this equation.

Both creatine and creatinine are very weak bases and in pure aqueous solution are not appreciably dissociated, that is, the value of C_{OH^-} is always large as compared with the dissociation constants of the two bases; accordingly these values represent the equilibrium between the undissociated molecules. It is

apparent that the temperature markedly affects the rate at which equilibrium is established. Myers and Fine (57) state that the equilibrium is attained at 36°C. only after eleven months, while Hahn and Barkan (58) find 2½ hours sufficient at 98°C. In the work cited above, the equilibrium had been established at 25°C. in 2460 hours, at 50°C. in 150 hours, at 70°C. in 70 hours and at 100°C. in 4 hours.

IN ACID SOLUTION

In acid solution of sufficient concentration creatine may be completely converted into creatinine. The destruction of the equilibrium state in acid solution is explained by Hahn and Barkan and by Edgar and Shiver on the assumption that the actual equilibrium is one between undissociated molecules, and that the apparent equilibrium is displaced by acids in the direction of the more dissociated base creatinine. Concerning the equilibrium conditions at intermediate hydrogen-ion concentrations no data at all are available before the work of Edgar and Shiver who have followed the progress of the reaction throughout the entire range.

Combining the above viewpoint with the simplifying assumptions employed in dealing with solutions of weak bases and their salts, the following expression has been derived for characterizing the effect of hydrogen-ion on the creatine-creatinine ratio:

$$\frac{m}{n} = \frac{K_2 \left(\frac{K_w}{10^{-pH}} + K_1 \right)}{\frac{K_w}{10^{-pH}} + K_2}$$

or more simply,

$$\frac{m}{n} = K_2 \left(\frac{K_1 + [\text{OH}^-]}{K_2 + [\text{OH}^-]} \right)$$

in which n and m are the total concentrations of creatine and creatinine in all forms, K_1 and K_2 their ionization constants and K_3 the equilibrium constant for their molecular species (as previously determined).

From these equations certain qualitative conclusions may be drawn immediately. Thus when K_1 and K_2 are small compared with C_{OH^-} ,

$$\frac{m}{n} = K_1$$

and when K_1 and K_2 are large compared with C_{OH^-} ,

$$\frac{m}{n} = \frac{K_1 K_2}{K_2}$$

These two equations represent the limiting equilibrium conditions in alkaline and strongly acid solutions, respectively. For intermediate concentrations, quantitative values for K_1 and K_2 are necessary.

TABLE 3
Comparison of experimental and calculated results

TEMPERATURE	pH	m/n CALCULATED	m/n DETERMINED
°C.			
50	1.00	36.72	38.08
	2.00	18.98	31.00
	3.00	4.01	3.61
	4.00	1.33	1.47
	5.00	1.05	1.11
	6.00	1.03	1.08

By the employment of buffer solutions the effect of hydrogen-ion between pH 1.8 and 6.2 on the ratio m/n has been experimentally determined at 50°C. These results are shown in table 3, the observed values of m/n at round pH values being read from a graph. The values given in the third column of the table are those calculated by means of the expression given above. The values of K_1 and K_2 were those given by Hahn and Barkan at 18°C., 1.85×10^{-10} and 4.6×10^{-12} , respectively. It is apparent that the agreement is on the whole fairly good. However, when the newly determined values of K_1 and K_2 at temperatures more nearly equal that of the experiment are substituted the agreement is not so good, due possibly to the undetermined effect of tem-

perature upon the constants, or more probably, to the fact that the relationship is exponential.

For pure aqueous solutions C_{OH^-} is always very large as compared with K_1 and K_2 , consequently the ratio m/n gives the true value for the equilibrium constant between molecular creatine and creatinine under such conditions. Any increase in C_{OH^-} , making the solution more alkaline, will not affect m/n , so that the same value for the equilibrium constant will be obtained in alkaline solutions as in aqueous solutions. In acid solution C_{OH^-} becomes negligible with respect to K_1 and K_2 and m/n reaches the limiting value, K_2K_1/K_2 . Using the values above, the ratio $K_1/K_2 = 46$, thus nearly all the creatine will be converted into creatinine in such a solution, the actual fraction depending upon the value of K_2 which in turn depends upon the temperature as noted.

Even if the values utilized for K_1 and K_2 are in error, examination of the equation derived above shows that the same type of variation of m/n with pH must obtain in every case. Thus it will be noted that the apparent equilibrium shifts very slowly up to the region of about pH 4. In the region between this value and pH 1, the shift is very rapid, the ratio m/n showing at this latter point a conversion of 97.5 per cent of the creatine into creatinine. From pH 1 to infinite acid concentration the shift again becomes very slow. From neutrality, pH 7, throughout the entire range of alkalinity, to pH 14, the ratio m/n is unchanging as noted above, and under the conditions of the experiment corresponds to a conversion of creatine into creatinine of about 50.8 per cent.

The conversion of creatine into creatinine under the influence of strong acids has long been known, but it has been only recently that quantitative studies have been undertaken regarding the velocity of the reaction. Hahn and Barkan were first to follow the course of the reaction, but confined themselves to a normal concentration of hydrochloric acid and a temperature of 26°C. Under these conditions the transformation of creatine into creatinine proceeded to completion and followed the course of a simple monomolecular change. Later Hahn and Meyer (59) indicated

that the velocity of the reaction in buffered solutions increased rapidly from pH 6 to pH 4.

A much more elaborate study of the kinetics of the reaction under various concentrations of hydrochloric acid and at several temperatures has been made by Edgar and Wakefield (60). A typical experiment is represented in table 4, with results for reaction-velocity constants calculated for a first order reaction.

The effect of temperature upon the velocity-constants may be calculated by substituting the values obtained at various temperatures in the Arrhenius equation, and solving for E. Thus

$$\frac{d \ln K}{d T} = \frac{E}{R T^2}$$

Calculation of E, the critical increment or heat of activation, leads to the value 20,000 calories which is for all practical pur-

TABLE 4
Reaction-velocity constants
Temperature 78°C. HCl 0.76 molar

	0 minutes	15 minutes	30 minutes	45 minutes	75 minutes	120 minutes
Conc. creatine, mol/l.	0.0300	0.0250	0.0208	0.0171	0.0114	0.0066
Vel. const., $K = 1/T \ln a/(a - x)$		0.0122	0.0120	0.0124	0.0127	0.0124

Average $K = 0.01235$.

poses independent of the acid concentration and the temperature. Integrating this expression there is obtained the equation,

$$\ln K = \frac{E}{R T} + C$$

where C, the constant of integration, has a value depending upon the concentration of acid. Converting to ordinary logarithms this becomes

$$\log K = - \frac{4368}{T} + C$$

from which at 0.19 N HCl, $C = 9.8496$; at 0.38 N HCl, $C = 10.1538$, and at 0.76 N HCl, $C = 10.5400$. Table 5 gives a comparison between the calculated results and those experimentally determined, and indicates the range of conditions covered by the experiments.

It is apparent that the agreement between the determined and calculated constants is fairly satisfactory. If the values of C are plotted against the acid concentration, values of the constant for any acid concentration may be obtained by interpolation, and the approximate velocity constant at any temperature may thus be obtained. From the data it is shown that the velocity-con-

TABLE 5
Comparison of results

TEMPERATURE	CONC. HCl	INITIAL CONCENTRATION CREATININE	K DETERMINED	K CALCULATED
°C.	mols/l	mols/l		
25	0.38	0.00750	0.000034	0.0000314
57	0.38	0.0300	0.000777	0.000824
78	0.19	0.00447	0.00256	0.00254
100	0.38	0.0075	0.02816	0.02780
78	0.38	0.0075	0.00494	0.00512
100	0.19	0.00367	0.01367	0.01380
78	0.76	0.0300	0.01235	0.01245
78	0.76	0.0150	0.01256	0.01245

stants increase with increasing acid concentration, the slope of the velocity-constant-acid concentration curve passing through a minimum at about 0.4 N HCl. It would thus appear that the velocity-constants are proportional to the hydrogen-ion concentration, although an exact comparison could not be made from the available data.

According to Cannan and Shore (61) the data fail to take into account the relationship between the hydrogen-ion concentration and the velocities of the reactions under the conditions in which the reaction is reversible. They argue that if the equilibrium be determined by the ratio of the concentrations of the undissociated molecules of creatine and creatinine, the velocities of the two opposing reactions should be governed by the same factors.

That is, the velocity should be inversely proportional to the hydrogen-ion concentration on the acid side of the buffer range of K_b , the basic ionization constant of either reactant, and should be independent of the hydrogen-ion concentration on the alkaline side. However, the available data indicate that the velocities are proportional to the hydrogen-ion concentration in solutions of strong acids, and inversely proportional in strongly alkaline solutions.

In an attempt to explain these discrepancies, the writer undertook a series of kinetic investigations in buffered solutions between pH 1 and pH 10. The velocity expression is put in the following form:

$$k_1 + k_2 = \frac{1}{t} \ln \frac{K_a}{K_a - (K + 1)x}$$

in which k_1 is the monomolecular velocity constant for the hydration of creatinine, k_2 that for the dehydration of creatine, K the equilibrium constant for molecular creatine and creatinine and therefore equal to the ratio k_2/k_1 , while a and x have their usual significance.

This expression may be utilized for the calculation of k_1 and k_2 provided K is known. By the employment of Edgar and Shiver's equations the value of K at 30°C. has been calculated as 0.6125. Making further use of these equations, Cannan and Shore relate K to C_{H^+} by an equation which, when k' values are substituted for k_b values ($pk' = pk_w - pk_b$), takes the form:

$$K = 0.6125 \frac{k'' (k' + C_{H^+})}{k' (k'' + C_{H^+})}$$

This equation has been utilized for calculating K at the various pH values of the reaction mixtures. Upon substitution of these values of K into the previously noted expression, with the corresponding velocity data, a reasonable constancy of the term $k_1 + k_2$ within a single experiment is obtained.

The data show that in solution acid to about pH 3 the conversion of creatine to creatinine is one of the first order, and is substantially irreversible. Furthermore, in following the course of

the reaction it was found that the relation of velocities to pH exhibited a well defined optima at about pH 3. The data for a typical experiment on the acid side of pH 3 is given in table 6.

TABLE 6
Rate of dehydration of creatine at 30°C.

pH = 2: K (Creatinine/Creatine) = 62.3: Conc. creatine 0.0106 M

t	a	x	$k_2 = 1/t \ln a/(a-x)$	$\frac{k_1 + k_2 = 1/t \ln Ka/[Ka - (K+1)x]}{K+1}$
25	100	1.97	80.0×10^{-5}	80.0×10^{-5}
75		5.58	76.4	76.4
125		9.12	76.4	76.4
170		12.25	76.8	76.8
385		24.33	72.5	73.1
865		46.18	71.5	72.9
1346		59.25	66.7	68.3
2017		76.92	72.7	75.2

TABLE 7
Rate of dehydration of creatine at 30°C.

pH = 3.77: K (Creatinine/Creatine) = 5.673: Conc. creatine 0.0106 M

t	a	x	$k_2 = 1/t \ln a/(a-x)$	$\frac{k_1 + k_2 = 1/t \ln Ka/[Ka - (K+1)x]}{K+1}$
25	100	7.29	304.0×10^{-5}	350.0×10^{-5}
50		15.39	334.0	398.0
75		21.77	327.0	393.0
125		31.93	308.0	377.0
170		38.17	283.0	350.0
385		64.62	269.0	370.0
695		79.98	232.0	405.0
1130		83.33	159.0	347.0
1896		85.00	99.0	370.0

In table 7 there is given the data concerning the velocity relationship on the alkaline side of pH 3, and a comparison of the values for k_2 and $k_1 + k_2$.

Cannan and Shore state that their data are chiefly valuable in showing that while the equations of Edgar and Shiver accurately interpret the equilibrium data they do not adequately define the velocity data. That is, the velocity constants are related to C_{H^+} in a manner not apparent in the equilibrium constant, a rela-

tion which is exhibited in a retarding effect of both velocities alkaline to pH 3. The writers infer that since this is not reflected in a change in the equilibrium constants, the factors responsible must be of equal effect upon the two reactions, and further that this same factor is responsible for changes in both k_1 and k_2 within this range.

Considering the data from pH 2 to pH 10, it has been possible to derive equations based on Edgar and Shiver's treatment, but involving three empirical constants, which define the relationship of k_1 and k_2 to C_{H^+} within the range pH 2-pH 10. In more strongly acid or alkaline solutions these equations are invalid. The equations follow:

$$k_1 = \frac{A' k' [C' + (H^+)]}{[k' + (H^+)] [C + (H^+)]} \quad k_2 = \frac{A'' k'' [C' + (H^+)]}{[k'' + (H^+)] [C + (H^+)]}$$

where $A' = 3.68 \times 10^{-3}$; $C' = 0.8 \times 10^{-3}$; $A'' = 2.25 \times 10^{-3}$; and $C'' = 1.9 \times 10^{-3}$. The calculated and observed values agree quite well within the range of pH indicated. It is pointed out that equations of this sort are of value solely in establishing an approximate summary of a mass of data, and it is particularly dangerous to attach any material significance to the empirical constants. However, Cannan and Shore are considerably nettled by finding that the value of C is identical with the dissociation constant of creatinine, and they state that it is difficult to see how the dissociation constant of creatinine can affect the intrinsic velocity of dehydration of creatine. The constants A and A' are the values which k_1 and k_2 would have were they determined only by the concentration of undissociated creatine and creatinine respectively.

A determination of the relative rate of transformation of creatine into creatinine in muscle extract, brain extract and of pure creatine in Tyrode's solution used for making extracts has recently been made by Hammett (62). According to this work, the velocity constant calculated from the equation for a monomolecular reaction for the transformation of creatine into creatinine in Tyrode's solution buffered to neutrality at 38°C. was found to be 0.00058. That for muscle extract similarly buffered

and otherwise under the same conditions was 0.00119, while that for brain extract similarly treated was 0.00104. The rate of creatine transformation into creatinine is thus twice as great for extracts of brain and muscle tissues, which are approximately equal, as for that of creatine in buffered Tyrode's solution.

IN ALKALINE SOLUTION

Creatinine is at least partially converted into creatine in alkaline solution, the reaction having served as a method of preparation of creatine from creatinine according to Benedict. The change may be induced by any free base whatsoever. Hahn and Barkan succeeded in demonstrating the fact that the reaction in alkaline media was a reversible one, in spite of the fact that both creatine and creatinine undergo a progressive decomposition in such media. By a series of approximations they measured the equilibrium constant, $K = (\text{Creatine})/(\text{Creatinine})$ at 26°C. in sodium hydroxide solutions ranging from N/1 to N/10. This value was found to be approximately 2.12, and it is interesting to compare this value with that of Edgar and Shiver at 25°C. in pure aqueous solution. The latter writers determined the reciprocal of Hahn and Barkan's constant, and this value 0.54 agrees extremely well with that obtained above, 0.47. The fact that K remained sensibly constant throughout a tenfold increase in alkalinity is a good indication of the validity of Edgar and Shiver's equations which require that the constant remain the same throughout the entire alkaline range.

Hahn and Barkan further show that the rate of change of creatinine into creatine corresponds to that of a reversible monomolecular reaction. Substitution of the data into the characteristic expression for such a reaction yielded for $k_1 + k_2$ a constant, the value of which measured in N/1 NaOH in time units of 1 hour was found to be 0.079 to 0.084. The velocity of the two opposed reactions varied with the CO_3H^- concentration, although a direct proportionality could not be established. Later Hahn and Fasold (63) found that the rate of transformation of creatine into creatinine progressively decreases as the alkalinity increases. This they explain by the assumption that it is the free creatine,

rather than creatine combined with base, that is involved in the conversion. Velocities predicted on this basis agree well with those observed, since as the concentration of free alkali is increased the quantity of free creatine arising from the hydrolytic decomposition of its alkali salt will decrease.

The rate of transformation of creatine into creatinine just on the alkaline side of neutrality is of considerable interest in any biological theory concerning the function of the two in metabolism. From the results of Cannan and Shore and those of Hahn and Meyer an interesting deduction may be made. Thus Hahn and Meyer found that at 38°C. in a solution of creatine of pH 7.01 a conversion of 1.32 per cent of the total creatine to creatinine was produced in 24 hours. This corresponds very closely with the creatinine in the adult urine as compared with the total body creatine. Thus, from this point of view, the origin of the creatinine in the urine is nothing other than the spontaneous dehydration of the creatine, and is governed by the active mass of creatine in the muscles, the temperature and the pH of the muscle. This is confirmed by the work of Cannan and Shore whose velocity constant for the conversion of creatine to creatinine at 30°C. and pH 7.2 is 0.000023, a value which becomes 0.000043 at 38°C. by application of the temperature correction of Edgar and Wakefield. This then corresponds to the dehydration of 1.03 per cent of the active mass of creatine per 24 hours, and is sufficient to account for the daily output of creatinine in the urine provided that the active mass of creatine in muscle is as great as 0.5 per cent. However, it now appears probable that only a small proportion of the creatine in living muscle is free, and it is very unlikely that the combined creatine is as readily converted into creatinine as the free creatine.

DISSOCIATION CONSTANTS

The various physico-chemical formulas characterizing the relationship of creatine and creatinine in various media are practically all concerned at one point or another with the ionization constants of the two substances. Considerable uncertainty has existed in the past concerning the ionization constants of these

compounds, Hahn and Barkan having reported at 17°C. the values 1.85×10^{-10} and 4.6×10^{-12} for creatinine and creatine respectively, while Wood (64) gives 3.57×10^{-11} and 1.81×10^{-11} at 40°C. Later work by McNally (65), Eadie and Hunter (66) and Cannan and Shore has led to the establishment of more concordant values. Several independent methods were employed in the determination of these values and the general agreement among them does much to enhance their value. In table 8 are listed the results obtained by the several investigators at the various temperatures employed.

TABLE 8
Basic ionization constants of creatine and creatinine

TEMPERATURE	CREATININE $K_b \times 10^{-12}$	AUTHOR	CREATINE $K_b \times 10^{-12}$
°C			
15	4.70	Cannan and Shore	
17	1.85	Hahn and Barkan	4.8
17		Cannan and Shore	2.8
20	6.40	Eadie and Hunter	9.6
25	7.00	McNally	
25	7.60	Cannan and Shore	5.5
30	1.50	Cannan and Shore	7.4
30	9.80	Cannan and Shore	7.4
40	10.10	McNally	
40	0.357	Wood	18.1

Thus certain differences exist between the values of different observers which cannot be explained as differences in temperature. The result for creatinine at 40°C. as reported by Wood is obviously incorrect, due as McNally points out, to the difficulty of carrying out measurements involving the rate of hydrolysis of methyl acetate at so high a temperature and at such low acid concentration. The first value for creatinine at 30°C. as given by Cannan and Shore is evidently a typographical error.

From the standpoint of its chemical behavior considerable interest attaches to the electrolytic dissociation of creatine. Its constitution indicates that it is an ampholyte, the conventional formula containing both an amino-group and carboxyl. In its

chemical behavior only the properties of a base are exhibited, and this but slightly as its ionization constant shows. Nevertheless in certain of its reactions it appears to be dissociated as an acid. Thus Hahn and Fasold found that creatine is more soluble in dilute sodium hydroxide than in water, 3.148 per cent in N/1 NaOH at 12°C. and 1.48 per cent in water, indicating a degree of hydrolysis of the creatine-sodium salt of 0.47, and therefore corresponding to an acid dissociation constant for creatine of $K_a = 5.2 \times 10^{-15}$. This is to be compared with its basic dissociation constant at 17°C, from which it is noted that creatine is about 1000 times weaker as an acid than as a base. Cannan and Shore find it difficult to justify on the grounds of organic chemistry the allocation of the first dissociation constant of creatine to the amino-group, and the assignment of purely negligible acid properties to the carboxyl group. They feel that a more likely interpretation would follow the application of Bjerrum's treatment of the amino-acids, the first constant ($k_1' = k_w/k_b$) becoming the acidic constant and the second (k_2'), the association constant of the basic group. Certain difficulties are inherent in such a view, and in any case, no clearer coordination of the dissociation constants with the physico-chemical data is obtained from this point of view.

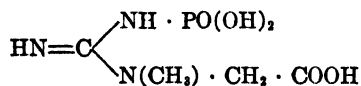
CONVERSION MECHANISM IN VIVO

The physico-chemical conditions governing the mutual conversion of creatine and creatinine *in vitro* have been fairly thoroughly established, as the foregoing indicates, while the direct application of the same principles to the transformation *in vivo* have not been eminently successful. The chief seat of creatine and creatinine in the body is the muscle and urine respectively, and the function of creatinine as an end product and derivative of creatine is accepted. This being the case the simplest application of the physico-chemical data would lead to the view that the mechanism *in vivo* is a simple dehydration of creatine, governed solely by the pH, the temperature and the creatine content of muscle. A necessary consequence of this view is that the creatine of the muscle be free, that is, present as such, otherwise

it may exist in such a state as to be incapable of direct conversion to creatinine.

The evidence has been accumulating for some time indicating that the greater portion of creatine in muscle is not present as such. Numerous investigators have postulated the existence of a creatine-containing complex, but until quite recently no such substance has been identified. In any case, if such a complex exists the data would seem to require that it be a combination of the loosest possible kind. It was, therefore, with greatest significance that Fiske and Subbarow (67) reported final success in isolating such a creatine complex in muscle.

According to this work and that later reported in confirmation by Eggleston and Eggleston (68) the compound consists of one molecule of creatine and one molecule of phosphoric acid, phosphocreatine according to the one and phosphagen according to the other. It is readily hydrolyzed in acid medium and has heretofore evaded discovery in that the usual conditions for the determination of phosphorus in muscle caused its destruction with the phosphorus appearing as inorganic phosphorus and the creatine as such. Fiske and Subbarow find its calcium salt to have the composition $C_4H_8O_5N_3Ca \cdot 4H_2O$, and suggest as its most probable structure,



They point out that its most characteristic chemical property, marked instability in acid solution, is characteristic of the few other compounds containing the group $-\text{NH} \cdot \text{PO}(\text{OH})_2$. It is the first substance in which phosphorus is attached to nitrogen to be isolated from natural sources, and the instability of the phosphamic group makes it one of considerable biological importance.

Fiske and Subbarow have determined the second dissociation constant of phosphagen by titration of the calcium salt with acid, and find $k_2' = 2.5 \times 10^{-5}$, a value some 250 times as great as the corresponding constant of o-phosphoric acid. This is due to the unmasking of the carboxyl group and indicates that one of

the functions of phosphagen in muscle is to neutralize a considerable portion of the lactic acid formed during muscular contraction. Their data indicate that the third constant is considerably less than 10^{-7} , and subsequent calculations show that the hydrolysis of phosphagen liberates sufficient base to neutralize the lactic acid formed up to a concentration of about 0.23 per cent. This hydrolysis would then seem to be the principal factor in permitting contraction of muscle to a limited extent without fatigue.

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A SYMPOSIUM ON MOLECULAR CONSTITUTION

AN INTRODUCTION

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The choice of molecular constitution as the subject for this symposium requires little explanation, for it has long been one of the goals of chemistry to devise models to account for the properties of substances in terms of structure. Although interest in molecular constitution was awakened in 1803 by the formulation of Dalton's brilliant but incomplete atomic theory, the first satisfactory contributions were the result of the principle enunciated in 1811 by the physicist, Avogadro. Unfortunately this principle was not fully comprehended by the scientific world until resurrected by Cannizzaro in 1858 in his masterly presentation. Cannizzaro not only gave a clear and illuminating distinction between atoms and molecules, but also established a method of settling for all time the vexed question of the number of atoms in a molecule.

We are all familiar with the rapid and systematic development which chemistry enjoyed in the years following the reading of this famous paper at Karlsruhe. This growth was due in no small measure to the development of a structural chemistry in which the classical concept of valence—the result of the combination of Avogadro's physical principle with the chemical laws of multiple proportions by whole numbers—played the leading rôle.

However, if we except the special contributions of Le Bel and van't Hoff on stereoisomerism, we must admit that the *methods* for attacking the problem of molecular constitution have remained, until comparatively recent times, essentially those

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established in 1858. Certain notable contributions, such as Wislicenus' idea of geometrical isomerism and Werner's coördination number, were made in the intervening years, but the methods which they employed to establish their propositions did not involve the introduction of fundamentally new principles. They made the best of what they had. The later illumination was lacking.

On the other hand, modern physics, which looks upon matter as an assemblage of positive and negative electricity organized in accordance with quantum rules, and the molecular characteristics primarily as a manifestation of the attractive and repulsive forces that arise from these specific distributions of electricity, has given the chemist a new viewpoint. From this he may profitably resurvey the problem of molecular constitution.

At the same time, modern physics has furnished many new tools with which the problem can be attacked afresh. I refer particularly to the x-ray, the spectroscope (in terms of the Bohr-Einstein frequency condition) and the determination of electric moments through refined measurement of the dielectric constant. To keep the symposium within reasonable compass it has seemed advisable to restrict the subject matter to a discussion of results which may be obtained from these three methods of analysis. Limitations of space and time also demand that these sub-topics be further limited in their scope. In this introduction we can only point out some of the salient features of the papers which follow.

In the first paper, Dr. Langmuir extends his well-known work of 1916 on the constitution of liquids and solids as manifested in surface tension and the behavior of surface films, by considering the molecular forces involved from the viewpoint of their electrical origin as developed by Debye in 1920 and in later papers. The effects of these molecular fields may be classified as (1) segregation, (2) orientation, and (3) deformation. Segregation is manifested most conspicuously in electrolytic solutions, but inasmuch as solutions have been the subject of two recent symposia, while orientation and deformation have not been previously discussed, these latter topics will constitute the

themes of the more detailed papers by Professors Smyth and Williams.

The x-ray having settled many of the simpler questions of constitution in the solid state, Professor Jaeger now utilizes this instrument to elucidate the more complicated question of the structure of the ultramarines, where we find many puzzling examples of change in color and composition arising from methods of preparation. In his paper, which appears in full in the Transactions of the Faraday Society, he shows that the ultramarines have a structure similar in many respects to the base exchanging zeolites and that the color is associated with the position of the sulfur atom in the mass.

When applied to liquids, the x-ray method yields only diffuse halos on a photographic plate instead of the sharp lines obtained from crystals. Most physicists have let the matter go at that. Professor Stewart now finds that he can partially resolve these halos by using more refined methods, and it is comforting to learn that the lengths and thicknesses which he computes for the hydrocarbons using Bragg's law check up satisfactorily with those deduced earlier by Langmuir and Harkins using surface tension methods. Checks obtained from methods involving such radically different principles as these should foster greater confidence in the conclusions reached.

From studies of reactivity, the organic chemist has known for a long time that certain groups like the methyl group, although non-ionogenic, can be classified as more or less positive in an electric sense, whereas others, like the nitro group, can be considered more or less negative without being construed as electrolytes. Again, the positions of these groups when substituted in the benzene ring have a marked bearing upon the physical properties of the molecules formed. Another important step in advance is explained in the papers by Smyth and Williams on electric moments. They regard radicals like CHO, COOH, NH₂, CH₃, OH, NO₂, and the halogens, as having the properties of an electric vector which is directed into space rather than in a plane, and are able to assign to this vector characteristic positive or negative values. Such values are quantitative measures of

the polarity of each radical. When we bear in mind that heretofore only qualitative measures of polarity were available, this step from qualitative to quantitative interpretation speaks for itself.

In the main all of the papers discussed thus far may be said to have confirmed, and rendered more precise in detail those pictures of molecular structure which have been generally accepted on classical grounds for a number of years.

Ever since 1913, when Bohr gave his famous formula for connecting the energy levels of atoms with the frequencies of absorbed or emitted light, which furnished the key that unlocked the wonderland of spectroscopy to the chemist and physicist, it has been clearly evident that the most searching analysis of chemical structure would ultimately be furnished by the spectroscope. Such a vast number of problems within this field immediately presented themselves to physicists that they had to spend most of their time unravelling the complexities of the line spectra of the atoms. They have had to postpone until very recently the interpretation of the highly complex band spectra; a subject of more pressing interest to chemists, because band spectra are produced by atoms linked together in molecules. It opens the way to a far broader field of inquiry and to more practical enlightenment.

Briefly stated, we may say that modern theory, as exemplified in the wave mechanics, enables one to describe the atom and its behavior in terms of integers, called quantum numbers. In his paper Professor Mulliken shows how these numbers change when simple atoms are brought together to form molecules. In this process there is a change in energy. If it decreases we have a stable molecule; otherwise it will be unstable. The energy values associated with the combinations of the lines in the bands enable one to follow these changes in detail and to calculate their respective probabilities, and also the number and strengths of the valence bands involved.

Perhaps the most remarkable result is that we can calculate the heats of dissociation of diatomic molecules like H_2 and I_2 far more accurately than we can measure them by the most refined

thermochemical methods at our disposal. Nor is this all. Band spectrum analysis has predicted that if oxygen has isotopes of mass 17 and 18, certain lines should be observed. The predicted lines have since been observed by Giaque and Johnston in intensities corresponding to roughly 0.1 per cent and 0.01 per cent of these isotopes in ordinary oxygen.

Still more striking was the prediction of Heisenberg that two allotropic modifications of hydrogen molecules should exist. This prediction was based upon the calculated energy differences which result from combining hydrogen atoms with parallel and antiparallel magnetic moments resulting from the spins of their protons. Shortly thereafter, Dennison on this assumption was able to account satisfactorily for the anomalous specific heat curves of hydrogen, and experimentalists at once began to investigate if hydrogen, which we have always called a pure substance, really is a mixture of two isolable types. Within a year Bonhoeffer and Harteck, and Eucken, as well as others, were able to produce in almost any desired quantity samples of hydrogen which showed different vapor pressures, melting points, and thermal conductivities.

Surely such tangible results mean important things in chemistry. They make us more ready to accept the statement that molecules like CH , NH , OH and even He_2 , which appear to break every classical rule of valency, exist in flames, arcs and discharge tubes, and that some of the molecules of sodium vapor are diatomic.

In interpreting optical rotation comparatively simple geometrical concepts have sufficed, but the problems with which modern chemistry has to deal are far more complicated. It is not surprising that it is necessary to approach the subject of molecular spectra armed with a far more advanced mathematical and physical background than was necessary to grasp stereoisomerism. Those who have mastered the intricacies of band spectra say that the primary difficulty in presenting the subject arises more from the reader's unfamiliarity with the methods and the notation which are necessary to represent the phenomena than from any real difficulty in comprehending the principles involved.

This extensive shift in chemical habits of thought from qualitative to quantitative concepts is accompanied by mathematical processes with which many chemists have not made themselves familiar. The processes have therefore the shock of unfamiliarity. But I verily believe that the difficulties presented by these newer methods are really not serious and that they will soon become so widely mastered as to become common knowledge among chemists. The mental digestion of anything new is usually a painful process; but the pains as well as the difficulties disappear when the novelty wears off and the "stunt" becomes common practice.

FORCES NEAR THE SURFACES OF MOLECULES

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In the early development of the kinetic theory, during the last century, it was usual to consider the molecules of gases as rigid spheres, which exerted no forces on one another except at the instant of contact. In this way it was possible to account quantitatively with fair accuracy not only for the effects of pressure and temperature on the volume, but also for the viscosity, heat conductivity, and diffusion of gases, and other phenomena involving the free paths of the molecules.

By considering also attractive forces which varied with some power of the distance between the centers of the molecules, van der Waals was able to account for the main features of the transition from the gaseous to the liquid state, and also explained in a satisfactory manner the departures from the ideal gas laws which are shown by all gases at high pressures.

As new properties of matter are brought into consideration, or as a deeper understanding of them is needed, it is necessary to postulate additional properties of the molecules, and to know more accurately the nature of the forces acting between them. For example, to deal with the properties of electrolytes it is necessary to consider electric charges on the molecules or ions. In 1912 Debye showed that the electrical properties of many dielectrics could be accounted for by assuming that the center of gravity of the electrons in a molecule did not coincide with the center of gravity of the positive charges of the nuclei. Thus the molecule possessed what we call a dipole moment, which can be measured as the product of an electric charge by the distance through which it is displaced. It is found, for example, that a molecule of water possesses a dipole moment of 1.8×10^{-18} electrostatic units. A moment of this magnitude could be

produced by having an electron at a distance of 0.37×10^{-8} cm. from a proton. Since there are 10 electrons in a water molecule, it is only necessary that the center of gravity of these electrons shall lie at a distance of 0.037×10^{-8} cm. from the center of gravity of the three nuclei in the molecule. Thus displacements of the electrons to distances minute compared with the diameter of the molecule can account for even the largest values of dipole moments that have been observed.

H. B. Hardy (1) in 1912 and the writer (2) (3) in 1916 pointed out that the fields of force around many chemical molecules must be very unsymmetrical, and that this resulted in an orientation of the molecules at the surfaces of liquids and in adsorbed films on solids. It was also found that the shapes which the molecules could assume, and which were determined by their chemical structures, were of great importance in connection with such properties as surface tension.

Within recent years, particularly through the work of Debye and his students, a great deal of knowledge has been accumulated regarding the electrical forces in liquids and solutions which contain ions and dipoles. Particularly in the study of electrolytes has this work cleared up many of the most serious difficulties of earlier theories.

There is now no need of drawing distinctions between chemical and physical forces. The chemist recognizes that many of the forces with which he has been dealing are electrical in nature, for, after all, molecules are built up of electrons and positive nuclei, and their interactions must necessarily be electrical. However, the simple classical theory of electrical forces based on Coulomb's law is wholly insufficient to account for chemical properties. With charged particles obeying Coulomb's law only, the minimum of potential energy is obtained when the positive and negative particles coincide. There must be something corresponding to repulsive forces holding the particles apart.

REPULSIVE FORCES BETWEEN MOLECULES

In many of the later developments of the kinetic theory where the molecules were regarded as rigid spheres, the repulsive forces

which must counteract the attractive forces were assumed to act only during collisions—that is, at the instant of contact of the spheres (4). No explanation was attempted of the internal forces within the molecule which could result in this repulsion between molecules.

In order to account for the compressibility of solids, Born and Landé (5) have assumed that the repulsive force between molecules (or ions) varies inversely as a power of the distance between the centers of the molecules. Thus in the case of halide salts of the alkalies, such as NaCl, KI, etc., they showed that the compressibility indicated that the repulsive force varied inversely as the tenth power of the distance, while the attractive force resulting from the charges on the ions varied inversely as the square, in accord with Coulomb's law. Born (6) also attempted to show that the inverse tenth power law for repulsion could be deduced by assuming that the electrons and the ions were arranged with cubic symmetry as at the corners of a cube. This attempt, however, must be regarded as a failure for two reasons. First, the method of mathematical expansion which was used is not legitimate when applied to distances as short as those between ions in salts; and, second, Born assumed that the cubical ions were all orientated so that their edges were parallel. This kind of orientation would be unstable under the forces assumed, for these forces would tend to orientate one cubical ion so that its corner would come opposite the face of another ion, and in this case the repulsive force would be replaced by an attractive force which would act in addition to the force between the ionic charges. Although such orientation of ions as Born assumes might conceivably exist in solid crystals from causes which he does not discuss, it is clear that it cannot be the cause of the repulsive forces, since the elimination of the orientation by melting the salt does not greatly alter the density or the compressibility.

Debye (7) has developed a theory which seems to give a better picture of the repulsive forces. Assuming the electrons to move in orbits in accord with Bohr's theory, he finds that the electric field around a molecule is a pulsating or partly oscillating field increasing in amplitude very rapidly as the surface of the molecule

is approached. Thus when an electron approaches a molecule it acquires, in addition to any motion of translation it may have, an oscillatory motion due to the pulsating field. Debye shows that this oscillatory motion tends to be 180° out of phase with the field producing it, and then shows, that because of the non-uniformity of the electric field near an atom the resulting force will be one of repulsion.

On this theory the repulsive forces between molecules are due to the perturbations in the electron orbits in one molecule, caused by the motions of the electrons in their orbits in the neighboring molecules. The repulsive force thus does not originate from a molecule as a whole, but comes from the close approach of electrons in the two molecules. This would seem to indicate that we may profitably regard these forces as *surface forces*, and should express them as functions of the distances between the surfaces of the molecules rather than in terms of the distances between the centers. This conception affords a justification, to a large extent, of the theory which regarded molecules as rigid elastic spheres.

Even if we accept Debye's picture of the origin of repulsive forces, we see that it really only refers the cause back to the quantum theory, by which the stable orbits of the electrons in the molecule are determined. At present, however, problems of this kind are treated by wave mechanics instead of by a consideration of orbits of electrons. For a few simple cases, such as interactions between hydrogen molecules, Hund and London have been able to calculate the forces by means of wave mechanics. But it will probably be a long time before definite knowledge of repulsive forces can be obtained in this way for more complicated molecules.

The quantum theory teaches that each electron in an atom is characterized by four quantum numbers, which are integers. Not all quantum numbers are possible; there are, for example, certain conditions (selection rules) which they must satisfy. The normal atom or molecule, with which the chemist is concerned, is one in which the electrons are so arranged that the total energy is a minimum, subject to the quantum rules that must be fulfilled.

It seems that the factor of greatest importance to the chemist

is that which is known as the Pauli principle, which states that no two electrons in an atom can have the same combination of four quantum numbers. It is this principle which underlies the Periodic Table of the elements, and in a similar manner determines the arrangement of electrons in a molecule. It is through the development of methods of this kind that our greatest hopes lie in obtaining a better understanding of the nature of repulsive forces.

For most practical purposes it is best for the chemist to regard molecules of organic substances as having shapes suggested by chemical structural formulas, and as having surfaces which are rather rigid so that strong repulsive forces are called into play for only moderate deformations. For many purposes it is still useful to look upon the surfaces as completely rigid.

ATTRACTIVE FORCES BETWEEN MOLECULES¹

Whereas the quantum theory seems essential in an understanding of the repulsive forces, the classical laws, such as the Coulomb law, are largely sufficient for dealing with the attractive forces between molecules. For example, the Debye-Hückel theory of electrolytes (8) is based on the Coulomb law, the Poisson equation, and the Boltzmann equation—all laws of classical mechanics.

In discussing forces between molecules, Debye has classified molecules in three groups: "(1) ionic, (2) polar and (3) non-polar." The ionic type is represented by electrolytic ions, such as K^+ , NO_3^- , etc., and gaseous ions. In these molecules the number of electrons is unequal to the number of positive charges of the nuclei of atoms, so that the molecule as a whole has an electric charge which is some multiple of e , the charge of an electron. The polar type is represented by molecules which have a dipole moment—that is, uncharged molecules in which the center of gravity of the negative charges does not coincide with that of the positive. Non-polar molecules thus include all molecules which

¹ The term "molecule" is to be used in its broad sense, which includes atoms and ions.

are uncharged and in which the centers of gravity of the positive and negative particles coincide. From Debye's point of view such molecules may correspond to quadrupoles, octopoles, etc. For example, positive and negative charges arranged alternatively at the corners of a square will give a quadrupole, at the corners of a cube an octopole. In forming clear conceptions of the attractive forces between molecules it is useful to consider the actual magnitude of the forces involved.

Ions

The electric field at a distance r from a univalent ion having a charge e is $e/\epsilon r^2$, where ϵ is the dielectric constant of the medium. The charge of the electron, e , is equivalent to 1.43×10^{-7} volt centimeter and thus the electric field is $1.43 \times 10^{-7}/\epsilon r^2$ volts per centimeter, and the electric potential corresponding to this force is $1.43 \times 10^{-7}/\epsilon r$. If we take for r the value 3×10^{-8} cm., which corresponds roughly to the distance between two ions in contact, we find the electric field to be 1.6×10^8 volts per centimeter and the potential to be 4.8 volts. Taking for ϵ the value 80, corresponding to the dielectric constant of water, we would obtain values only one-eightieth of those given. However, it is doubtful if the conception of dielectric constant is entirely justified at distances as short as this for we can hardly speak of two molecules in contact as being in a medium having known electrical properties. At distances several times greater than the molecular diameter the use of dielectric constant in this way is justified.

The applications of the Debye-Hückel theory to electrolytes prove that the forces at these larger distances are of vital importance in an understanding of the properties of ions. According to the Coulomb law the force between two ions varies inversely as the square of the distance. In electrolytic solutions the increased concentration of positive ions around negative ions, and vice versa, causes the force between two given ions to decrease with increasing distance more rapidly than according to the inverse square law.

Polar molecules

At a distance r from a dipole molecule having an electric moment μ the electric potential is $\mu \cos \theta / r^2$, where θ is the angle between the radius vector r and the axis of the dipole. It can thus be found that at a distance r along the dipole axis the electric field is $-2\mu/r^3$, this force being in a direction of the polar axis. At a distance r in the equatorial plane of the dipole the electric force is also in a direction parallel to the polar axis but has the magnitude $+\mu/r^3$.

Debye (9) has shown that in general because of thermal agitation a dipole (or quadrupole) molecule in a gas or liquid is changing its orientation so fast that we must not regard the force produced by a dipole as a steady force, but a rapidly fluctuating force, and under these conditions many of the effects produced by the force are proportional to \bar{E}^2 or the mean square field. The effective force can thus vary inversely as the sixth power of the distance from the dipole.

Non-polar molecules

If the molecule is a quadrupole the instantaneous force in any given direction will vary inversely as the fourth power of the distance, and thus the effective fluctuating force will vary inversely as the eighth power of the distance. With more symmetrical molecules the forces will vary inversely with still higher powers of the distance.

Under the influence of forces of the kinds we have been considering the various types of molecules in liquids respond in different ways. Positive ions tend to concentrate around negative ions in the manner considered by the Debye-Hückel theory (8). Dipole molecules tend to be orientated by the field in the neighborhood of the ion. Thermal agitation tends to prevent this orientation, so that only when the dipole molecule is very close to the ion is the orientation of the molecule complete.

The dipole molecule, orientated in a field, tends to move in the direction towards which the field is of greater intensity. The change in potential energy is mE , where E represents the change

in field strength and m is the effective dipole moment (average moment) in the direction of the field.

A field insufficient to orientate the dipoles completely gives an effective dipole moment m , which according to Debye (10) is

$$m = \mu^2 F / 3kT$$

where F is the electric force tending to produce the orientation. Since the energy available for producing motion of translation in a dipole is proportional to mF , we see that at large distances dipoles attract one another in proportion to F^2 and therefore in inverse proportion to the sixth power of the distance. If, however, we consider a fixed dipole (for example one attached to a large organic molecule) acting on another dipole at a very short distance so that the latter is orientated by the field of the former, then the force of attraction will vary inversely as the fourth power of the distance.

An electric field of intensity F , acting on a non-polar molecule, causes a deformation, or polarization, of the molecule so that it acquires a dipole moment m given by

$$m = \alpha F$$

where α is the polarizability. A liquid made up of non-polar molecules of this kind will have a dielectric constant ϵ which is greater than unity, and the *molar polarization* of the liquid is calculated from ϵ by means of the equation

$$P = \left(\frac{\epsilon - 1}{\epsilon + 2} \right) \frac{M}{\rho}$$

where M is the molecular weight and ρ is the density of the liquid. The relation between P and α is given by the equation

$$P = \frac{4}{3} \pi N \alpha = 2.54 \times 10^{24} \alpha$$

where N is the Avogadro number, 6.06×10^{23} . The quantity P has the dimensions of a volume and is thus measured in cubic centimeters. For ordinary organic liquids the value of P is roughly about 0.3 of the volume of a gram-molecule. A few

values of P and α are given in table 1. From the value $\alpha = 10^{-23}$, which is of the order of magnitude found in most organic liquids, we can calculate that the electric field needed to give to a non-polar molecule a dipole moment of 10^{-18} is $F = 3.0 \times 10^7$ volts per centimeter. This is the field that would exist at a distance $r = 7 \times 10^{-8}/\sqrt{\epsilon}$ cm. from an 'electron. A field of this magnitude would be found at the distance $r = 2.7 \times 10^{-8}/(\epsilon)^{\frac{1}{2}}$ in the direction along the axis of the dipole.

From the foregoing discussion, we see that the effects of the electric fields of molecules are of three kinds which we may classify as (1) segregation, (2) orientation, and (3) deformation. As an example of segregation, we have the segregation of positive ions around negative ions in electrolytes. Dipole molecules become

TABLE 1
Values of P and α

	P	α
	cc.	
H ₂	5.8	2.28×10^{-24}
N ₂	13.6	5.4
CH ₄	21.0	8.3
C ₆ H ₆	25.8	10.2

orientated in the field produced by any other molecule and thus are attracted toward the molecule producing the field. Non-polar molecules, under the influence of fields of other molecules, become deformed or polarized so that they acquire a dipole moment in the direction of the field and are thus attracted by the molecule producing the field.

In estimating quantitatively the magnitude of the segregation and orientation that result from molecular fields, we may apply the Boltzmann equation;

$$\frac{n_1}{n_2} = A e^{\lambda/kT}$$

where n_1 and n_2 represent the relative numbers of molecules in two given positions, or orientations, and λ is the work done in transferring a molecule from one of these states to another.

The constant A involves the ratio of the *a priori* probabilities of the molecules in the two regions or states under consideration. These probabilities are frequently dependent upon geometrical factors, but often involve a knowledge of the quantum phenomena accompanying the change in state. The quantity ϵ in this equation is the base of the natural system of logarithms, 2.718; k is the Boltzmann constant, 1.37×10^{-16} erg per degree; T is the absolute temperature.

We see from the Boltzmann equation, that when the constant A is not too far removed from unity, the effects of segregation and orientation usually begin to be important only when the energy λ becomes of the same order of magnitude as kT . At room temperature the value of kT is 4.1×10^{-14} erg, which is the energy that an electron would acquire in falling through a potential of 0.025 volt.

In Debye's theory for the contribution of dipole molecules to the dielectric constant of liquids, it is shown that the effective dipole moment m of the dipole molecules (of moment μ) is $\frac{1}{2}\mu$ when the field is of such intensity that the work done by the field in orientating the molecule is equal to $2kT$.

The segregation of ions of one sign around an ion of the opposite sign will be marked at distances r less than that at which the potential is 0.025 volt; that is, when r is less than $57 \times 10^{-8}/\epsilon$ cm. If ϵ has a low value, of a few units only, then even in very dilute solutions, where the distances between the ions are more than ten times greater than the molecular diameters, the ions will tend to be swept out of the solution and brought into contact with each other. This is in accord with the fact that such salt-like substances as NaCl, whose crystals are held together by forces of the Coulomb type, are practically insoluble in organic liquids of low dielectric constant. On the other hand, in water and other liquids of high dielectric constant, in solutions of even moderate concentration, the ions are far enough apart so that their potentials with respect to one another are less than kT , which agrees with the fact that these salts are soluble in these liquids, and that their solutions behave as electrolytes.

We have seen that to orientate the larger portion of dipole

molecules in liquids requires a field F which makes μF greater than $2 kT$. This means that a field of about 2.4×10^7 volts per centimeter is needed for the orientation. The work done when the orientated molecule is brought into the field is of the same order of magnitude, so that a field sufficient to cause nearly complete orientation of dipole molecules will also cause marked segregation. A field of 2.4×10^7 will exist at a distance $r = 8 \times 10^{-8}/(\epsilon)^{\frac{1}{2}}$ cm. from a univalent ion, or at a distance $r = 3 \times 10^{-8}/(\epsilon)^{\frac{1}{2}}$ cm. along the axis of a dipole molecule having a moment $\mu = 10^{-18}$. In other directions than along the dipole axis the force will be less and therefore the distance at which effective orientation or segregation occurs will be less than that just given.

From these calculations we conclude that the interaction between dipole molecules of moment 10^{-18} can cause mutual orientation only when they are practically in contact. If they were separated by one additional molecule, so that the distance between centers is 6×10^{-8} cm., even if they were still orientated, the force would be only one-sixteenth as great, since it varies inversely as the fourth power of the distance. However, at this greater distance, the orientation would be far from complete, so that the force would actually vary inversely as the sixth power of r , and would thus be only one sixty-fourth as great as if the molecules were in contact.

The electric force necessary to deform a molecule sufficiently to give it a dipole moment $\mu = 10^{-18}$ (viz., 3×10^7 volts per centimeter) is practically the same as that needed to produce orientation of a dipole molecule having this same moment. Thus when two dipole moment molecules are in contact, the dipole moment which each possesses is practically doubled because of their mutual deformation.

Taking the electric field near a dipole to be proportional to r^{-3} , and remembering that the distance between the center of one molecule and the surface of its neighbor is only one-third the distance to the surface of the far neighbor, we realize that the electric field intensity at one side of the dipole molecule is twenty-seven times as great as at the opposite side.

The latent heat of evaporation of a liquid expressed per molecule

gives the energy which must be expended to separate the molecules of liquid from one another. Pentane, a non-polar liquid, which boils in the neighborhood of room temperature ($36^{\circ}\text{C}.$), has a heat of evaporation of about 40×10^{-14} erg per molecule, which is roughly equal to $10 kT$. According to the rough empirical rule of Trouton, the absolute boiling points of liquids are proportional to their latent heats of evaporation, so that in general, to the same degree of approximation, the heats of evaporation per molecule for all liquids will be about $10 kT$, where T is the temperature at the boiling point. This can be looked upon as a consequence of the Boltzmann law. The coefficient A in this case, however, is quite different from unity.

The energy involved in the close approach of ions to within molecular dimensions is far greater than $10 kT$ —at least when the medium is one of low dielectric constant. Thus we are not surprised at the fact that substances built up of ions are solid bodies which melt and boil only at very high temperatures, and are soluble only in liquids of high dielectric constant.

We have found that the energies involved in the approach of dipole and non-polar molecules (having values for μ of about 10^{-18} , and for α of 10^{-23}) to within a distance of 3×10^{-8} cm. is approximately equal to kT ($T = 300^{\circ}\text{K}$). Since a given molecule will usually be in contact with about a dozen others, it is to be expected that the energy necessary to separate a molecule from all its neighbors would be of the order of magnitude of $10 kT$. In fact, we can reasonably expect values larger than this because of the fact that the greatest effects will be produced in the deformation of the molecule on its side facing the adjacent molecule ($r = \frac{1}{2}$ molecular diameter), the electric field there being about eight times greater than at the center of the molecule.

We thus have an explanation of the fact that liquids whose molecules have the properties we have postulated will, in general, have boiling points considerably above room temperature. When the molecules are in contact the energies of the non-polar molecules are not very greatly different from those of the dipole molecules—at least are of the same order of magnitude. In this we have an explanation of the fact that the boiling points of liquids

containing dipole molecules are only moderately higher than those of non-polar substances. It is possible, for example, to have liquids whose molecules are dipoles, such as anhydrous hydrogen chloride, which boil at temperatures far below room temperature.

Our analysis of the known electrical forces causing the interactions of molecules thus leads us inevitably to the conclusion that the forces involved in holding together the molecules of organic liquids are acting almost wholly between molecules *in contact*, and that in general no serious error would be made in neglecting all forces which act at greater distances. This conclusion is, I believe, thoroughly justified in the case of all liquids built up of non-polar molecules. It applies with reasonable accuracy to most liquids having molecules containing dipoles. But in general, where liquids contain free ions the range of the forces is much greater, and we must then take into account the Coulomb forces which act at greater distances.

For many years, in connection with studies of adsorption, surface tension, and the kinetics of heterogeneous reactions, the writer has found it extremely useful to explain these phenomena in terms of actions between molecules *in contact*. From an empirical point of view the results have justified this method of attack. In many ways this conception is in accord with chemical tradition, for the chemist has always considered that chemical action between molecules takes place between molecules in contact.

The physicist, probably ever since the time of Newton, has been rather inclined to consider forces which vary as some power of the distance, or to deal with fields of force which extend throughout space. The remarkable success of the physicist in the development of the atomic theory, and more recently, in some of the applications to chemical phenomena, such as those involved in the properties of electrolytes, seems to have made many chemists and physicists believe that these methods would also provide the solutions to more complicated chemical problems.

It must be emphasized, however, that the physicist, in attempting to calculate the manner in which dipole molecules or non-polar molecules will interact in liquids, meets problems which are

mathematically so complicated that it is necessary to make simplifying assumptions. For example, the potential energy of dipole or non-polar molecules with respect to one another is expressed as an infinite series in which the successive terms involve as factors $1/r$, $1/r^2$, $1/r^3$, etc. The coefficient of the first term for the case of dipole molecules is 0, the coefficient of the second term is then calculated with great care and often with great difficulty; and although the coefficients of the third and subsequent terms are known not to be zero, these terms are neglected because of the fact that they involve higher powers of r . We have seen, however, that the forces which are primarily important in liquids are those between molecules in contact, and that a small increase in the distance causes the forces to become very small. For example, with a force varying with $1/r^3$, such as Debye finds with non-polar molecules, the energy involved in the approach of two molecules would fall to one-half value if the distance between the molecules were increased 15 per cent. This change in energy has its effect in the exponent of the Boltzmann equation, so that most of the actions of importance must occur with only still smaller variations in the distance r . It is obvious, therefore, that even for the roughest kind of approximation one is not justified in neglecting the term involving $1/r^3$ in comparison with that which involves $1/r^2$.

As another example of the kinds of approximation that are necessary in treating mathematically the forces between dipole molecules, we have Debye's treatment of the relations between dielectric constant and chemical association (11). He considers the effect of dipoles on one another as the concentration of the dipolar molecule increases in a non-polar solvent. Assuming the molecules to be spheres, complicated equations are derived allowing for the interactions. The result is that the dipole moment per molecule increases with concentration because the molecules tend to line up along a common axis. This is due to the fact that the force along the polar axis is twice as great as in the equatorial plane for a given value of r . An analysis of experimental data, however, shows that in solutions of many dipole substances in non-polar solvents, the polarization per molecule decreases as

the concentration increases. Such a result could be explained if the molecule instead of being a sphere were ellipsoidal with the equatorial diameter less than 80 per cent of the polar diameter. The introduction of such a concept would introduce far too great mathematical complications to make an analysis worth while.

Perhaps the greatest objection to a mathematical treatment of the properties of liquids in terms of power laws of force is that it becomes practically impossible to take into account the effects resulting from the complicated shapes of molecules which must characterize organic substances, according to the structural formulas of the chemist. If now we assume that the forces between molecules come into play only at their areas of contact, we have simplified the problem mathematically to such an extent that we can take into account our knowledge regarding the shapes of the molecules which can be furnished us by the chemist. Of course, in so doing we are making approximations, but the errors so introduced will, I believe, usually be far less than those which are often made by the physicist in dealing with these problems. I should like to outline now the ways in which a conception of surface forces can be developed to give concrete pictures and quantitative results for many problems which are too difficult to handle by the method involving the power laws of force.

In considering that the interactions between molecules occur at their surfaces of contact, it is not necessary to assume that the nature of the forces at any given part of the surface is characteristic wholly of the atom underlying the surface. The chemist knows, for example, that the properties of an organic molecule are not simply the sum of the effects due to the separate atoms in the molecule. If one of the hydrogen atoms in the methyl group of acetic acid be replaced by a chlorine atom, the effect of the greater charge on the kernel of the chlorine atom as compared with that of the hydrogen atom which it replaces, is to displace the electrons in the carboxyl group in the direction towards the chlorine atom. This displacement of the pair of electrons which hold the nucleus of the hydrogen atom of the carboxyl group causes the hydrogen nucleus to be held less firmly, and thus makes it easier for the hydrogen nucleus to pass over to a water molecule

(in aqueous solutions of acetic acid) to form an OH_3^+ ion, which is the so-called hydrogen ion characteristic of acids. We thus have a clear indication of an alteration in surface forces which may extend over the whole surface of the molecule as a result of the replacement of a hydrogen atom by a chlorine atom.

We may form a clearer conception as to the magnitude of these changes in the surface forces due to effects transmitted from atom to atom in the molecule, by considering the chlorine-substituted fatty acids. In table 2 the values of the dissociation constant K for some of these acids are given as taken from Landolt-Börn-

TABLE 2
Dissociation constants of chlorine-substituted fatty acids

	K	$\ln r$	VOLTS
Acetic acid	1.85×10^{-5}	[0]	0
Chloroacetic	155.0	+4.44	0.1053
Dichloroacetic.....	5000.0	7.6	0.190
Trichloroacetic	20000.0	9.3	0.233
Propionic acid	1.4×10^{-5}	[-0.26]	-0.006
α -Chloropropionic.....	147.0	4.36	0.1045
β -Chloropropionic	8.6	1.53	0.0382
Butyric acid.....	1.5×10^{-5}	[0.21]	-0.0053
α -Chlorobutyric.....	139.0	4.30	0.1038
β -Chlorobutyric.....	8.9	1.57	0.0392
γ -Chlorobutyric.....	3.0	0.48	0.012

stein tables. In the third column, under the heading $\ln r$, is given the natural logarithm of the ratio of K for the acid in question to the value of K for normal acetic acid. According to the Boltzmann equation, this quantity should be equal to λ/kT , where λ represents the difference between the work necessary to remove a hydrogen ion from the given acid molecule and from an acetic acid molecule. Since kT is equivalent to 0.025 volt, we can obtain the value of λ in volts by multiplying the values of $\ln r$ by 0.025; the last column of the table gives these values.

Comparing the monochloro acids with each other, we see that all three of the acids in which the chlorine is in the α -position give

$\lambda = 0.105$ volt. The two acids with chlorine in the β -position give $\lambda = 0.039$ volt. The single γ -chloro acid for which data are available gives $\lambda = 0.012$ volt.

From theoretical considerations we should expect that any state of strain which is transmitted from atom to atom along a hydrocarbon chain should decrease exponentially as the distance increases. The above data thus leads to the conclusion that the electric polarization produced by the presence of a chlorine atom in a hydrocarbon chain decreases in the ratio 2.7: 1 in being transmitted from one carbon atom to the next. If instead of chlorine we should substitute other radicals, we might obtain electric forces of different magnitudes, but in any case we should expect this ratio 2.7: 1 to apply to the decrease in the force from atom to atom. A considerable effect is thus transmitted from one atom to the next, but very little is transmitted as far as the second or third atom.

This result justifies us in attributing definite properties to different parts of the surface of the molecules of aliphatic compounds. For example, the field of force around a carboxyl group in a fatty acid should be independent of the length of the hydrocarbon chain, provided that this is more than about two carbon atoms long. That is, the forces near the surface of the carboxyl group should be practically constant for all the acids higher than propionic acid and would be roughly the same in the case of acetic acid, but might be considerably different in the case of formic acid. Similarly, we should not be able with any reasonable accuracy to regard the field of force around the carboxyl group as due merely to the super-position of the effects of the hydroxyl group and the carbonyl group, for these two groups are too close together in the molecule to be without important effect on one another.

PRINCIPLE OF INDEPENDENT SURFACE ACTION

From the foregoing analysis of the forces acting between molecules of various types, we conclude that there is a large class of substances for which we are justified in regarding the forces between two molecules in contact as being dependent mainly on the nature of the surfaces of the molecules which are in contact.

This principle of independent surface action (12) will always be only an approximation to the truth, but there are many cases where it applies with sufficient accuracy and so greatly simplifies the problems of the interactions between molecules that useful results are obtained in problems so complex that no solution is otherwise possible. Let us consider some of these problems.

The theory of adsorption in monomolecular films on solids and liquids (13) is an example of the application of this principle. According to this theory, the force which holds an adsorbed molecule or atom on a surface depends on the character of the surface of contact between the molecule and the solid. If a second layer of molecules should form, the forces holding the molecule to the second layer are thus entirely different from those holding the molecules of the first layer. The rates of evaporation of the molecules from the first layer or from the second layer will differ greatly, especially since they depend upon the magnitude of the forces according to an exponential relation of the Boltzmann type. Two general cases must be considered. If the forces holding the molecules in the first layer are greater than those holding those of the second, there will be a wide range of pressures of the adsorbed gas for which the film will never exceed one molecule in thickness. We thus arrive at the conception that a certain fraction, θ , of the surface is covered by adsorbed molecules, and that the properties of this adsorbed film depend primarily on θ . If the forces between these molecules and the underlying surface are very large compared to those that act between adjacent molecules, then, for example, we may conclude that the rate of evaporation of the adsorbed molecules will be proportional to θ . This simple conception leads to an adsorption isotherm which has been found to hold experimentally in a large number of cases. However, if the forces that act between adjacent adsorbed molecules are not negligible, there will be large deviations from this simple law, but the theory may be easily extended to take into account such forces. The forces may be those of attraction, or, if the molecules become dipoles as a result of the adsorption, or if they become crowded, their interaction may cause repulsive forces.

The second important case (14) to be considered is that in which the forces that hold the second layer of molecules are greater than those which hold the first; or, more generally, the case in which the forces acting between adjacent adsorbed molecules are greater than those with which each of these is held on the underlying surface. There is then great difficulty in getting any appreciable number of molecules in the first adsorbed layer, and single molecules or atoms or groups of molecules in the first layer act as nuclei from which large aggregates or crystals may develop. The condensation of cadmium or mercury vapor on cooled glass surfaces is an example of this type. It is possible to formulate the problem quantitatively and to express the number of nuclei that will form per second as a function of temperature and pressure. The calculated values are in good agreement with those obtained by experiment. If definite numbers of isolated copper atoms are evaporated on to a clean surface, each one serves as a nucleus for the formation of cadmium crystals, when the temperature of the surface and the pressure of the cadmium vapor are carefully regulated, and thus by dark field illumination of the surface the copper atoms can be directly counted. Some experiments made several years ago by Mr. Harold Mott-Smith have shown that this method can be developed to count atoms just as the C. T. R. Wilson method can be used to count ions.

In case the adsorbed atoms on a metallic surface are electrically charged or acquire large dipole moments, electrical forces are brought into play which may make the principle of independent action inapplicable. For example, the rate of evaporation of electrons from a tungsten surface at high temperature is enormously increased by the presence of adsorbed thorium (15) or caesium (16) atoms on the surface. But the increase in the number of electrons which evaporate is not even approximately proportional to the amount of thorium or caesium which is present on the surface. The same is true for the evaporation of positive caesium ions from a tungsten surface. In both of these cases, the heat of evaporation of electrons or ions varies approximately linearly with θ , the fraction of the surface covered by the adsorbed atoms, and thus, according to the Boltzmann equation, the

logarithm of the rate of evaporation of electrons or ions varies linearly with θ . In the case of the evaporation of neutral atoms—for example, atoms of oxygen from adsorbed films on heated tungsten filaments—the rate of evaporation is much more nearly proportional to θ .

In studies of the surface tensions of organic liquids (2) (17) and of the properties of adsorbed films of organic substances on water (3) (4) and of oil films on water, the principle of independent action has proved itself particularly useful. It gives immediately a simple reason for believing that these films should rarely be more than one molecule in thickness; or rather, that if they are more than one molecule in thickness, their properties will be markedly different from those of films in which the surface is not completely covered with a single layer. The theory also gives immediately reasons for believing that adsorbed films of many organic substances on water will consist of orientated molecules. Thus the area on a water surface occupied by molecules of the various fatty acids is dependent on an interaction between the carboxyl group and the water, and is independent of the length of the hydrocarbon chain. This simple result, proved by experiment, demonstrates that the molecules are orientated so that the carboxyl group is in contact with the water, leaving the hydrocarbon tails to form a layer above the carboxyl group which will have the properties characteristic of a liquid hydrocarbon.

The theory is equally applicable in pure organic liquids. The total surface energies (surface tension extrapolated to the absolute zero) of hexane and of hexyl alcohol are practically identical. This is readily explained by the orientation of the molecules which prevents the hydroxyl groups from coming in contact with the surface, so that in both cases the actual surface is that of a pure hydrocarbon.

Studies of the surface tension of aqueous solutions of various aliphatic compounds in water prove that in concentrated solutions the surface becomes covered with a closely packed monomolecular film consisting of orientated molecules like those in oil films. With sufficiently dilute solutions, however, the amount of substance adsorbed in the surface is not enough to cover the whole

surface with closely packed molecules. Under these conditions, the hydrocarbon chain lies flat in the water surface and the energy needed to transfer any molecule from the surface to the interior increases by a definite amount for each additional CH_2 group in the hydrocarbon chain. This is an excellent example of the application of the principle of independent surface action, each CH_2 group producing its effect independently of the others.

Similar views prove useful in studies of many other properties of matter. Consider, for example, jellies made by amounts of gelatin or soaps in concentrations less than 1 per cent by weight. The elasticity proves the existence of a continuous frame-work of molecules in contact, extending throughout the liquid. The time of relaxation of such jellies serves as a measure of the rate at which the molecules which form the chains separate or evaporate from one another. Guided by these views, I made some experiments, over ten years ago, to determine the diameters of the cross sections of the fibers or rods that must be the elements of the rigid frame-work. For this purpose I made up some dilute gelatin jellies on filter paper and measured the rate at which water could be forced through the jellies by applying a definite pressure. By a modification of Stokes' law which gives the rate of fall of small spheres in liquids, it was possible to calculate the force necessary to move small cylinders of various diameters through a liquid. This law was then checked experimentally by measuring the rate at which water passed through a column of glass-wool having fibers of known size. Applying this law to the case of the motion of water through a gelatin jelly, it was thus possible to calculate the size of the fibers. Only rough experiments were made, but the results showed clearly that the diameter of the fibers was approximately 10^{-7} cm.

I believe that there is real justification for dealing with molecules of this character, at least as a first approximation, as though they followed the same laws as bodies of large size, such as the fibers of glass-wool. Einstein showed, years ago, that Stokes' law could be used, approximately, for the study of the rate of migration of ions through water solutions. I believe that a thorough quantitative study of the forces necessary to drive water through

various jellies should give much valuable information as to the structure of these jellies.

Very useful pictures of the mechanism involved in the viscosity of liquids and of diffusion in liquids and solids may be had by considering that molecules in contact exist in two states: one in which the surfaces are rigidly connected, the other in which they are entirely free to move. The behavior of the molecules is thus analogous to that of a gas condensing on a solid; the molecules of the gas strike the surface, remain adsorbed for a certain time, and then evaporate off again. Applying this conception to molecules in liquids, we see that the motion of the molecules past each other, involving viscosity and diffusion, depends upon the relative times during which the molecules are in this rigid, or in this mobile contact. These times can be calculated from an equation of the Boltzmann type in terms of the energy difference between the two states. This theory accounts for the frequent occurrence of temperature coefficients of viscosity and diffusion, which agree with the Boltzmann equation. It seems also to account for the fact that the viscosity of different members of a series of hydrocarbons increases in geometrical proportion to the length of the chain. It would seem that the principle of independent surface action should afford a means for the development of a simple theory of viscosity which would take fully into account the shapes and sizes of the molecules and of the different chemical groups contained in the molecules.

The principle has also found many applications in connection with the mechanism of heterogeneous chemical reactions. The interaction of oxygen and hydrogen and of carbon monoxide and oxygen at low pressures in contact with a heated platinum filament (18) has shown that equations which are based directly on this principle are in excellent agreement with the experimental results over very wide ranges of pressure and temperature. For example, the experiments showed that at low temperatures the reaction velocity was accurately proportional to the partial pressure of oxygen and inversely proportional to the pressure of carbon monoxide. This behavior could be completely accounted for by assuming that the rate of reaction was determined by the rate at

which oxygen molecules could reach holes in the films of adsorbed carbon monoxide which were left by evaporation of carbon monoxide molecules, or which were formed by the removal of the carbon monoxide by the oxygen which reached these holes. The poisoning effect of the carbon monoxide was due to the fact that the opportunity for the oxygen to reach the holes was decreased if the carbon monoxide molecules were able to fill up the holes before the oxygen arrived. It seems difficult to reach quantitative agreement with these experiments except by the application of the principle of independent surface action.

The interaction of hydrogen and oxygen in contact with tungsten filaments at temperatures ranging from 1500° to 2500°K is another illustration of a similar kind. Oxygen acts to form WO_3 at a rate proportional to the oxygen pressure (19). Oxygen atoms *in the adsorbed oxygen film* do not react with one another and with the tungsten to form WO_3 even at the highest temperatures. At 1500°K the life of oxygen atoms on the surface is of the order of years; at 1860°K it is about 25 minutes; and at 2070°K it is 15 seconds. When the atoms leave the films at the higher temperatures they do so as free atoms, not as molecules. Thus, even in the presence of minute pressures of oxygen, the tungsten surface is practically completely covered with a single layer of oxygen atoms. Oxygen molecules which strike this surface condense on it, but evaporate from this second layer at a relatively high rate; but while thus adsorbed, they move freely over the surface and are able to fill up any holes that form in the first layer. Also the molecules, while adsorbed in the second layer, have a certain probability of interacting with those of the first layer and with the underlying tungsten to form WO_3 , and the holes thus formed by the removal of oxygen from the first layer are soon filled up by the migration of the molecules of the second layer.

Hydrogen molecules are not able at any temperature to react directly with the oxygen in either of the first or second layers (10), but if they reach the tungsten at one of the holes in the first layer, they react immediately with the adjacent oxygen. Thus when the oxygen pressure falls to a certain low critical value, the hydrogen

completely removes all the oxygen from the surface, and it does this suddenly. The hydrogen which then strikes the film is dissociated into atoms to an extent that depends upon the temperature, and the atomic hydrogen formed goes to the bulb and reacts with the WO_3 which has previously been deposited there.

This theory which can readily be stated quantitatively appears to be in complete agreement with all the experimental facts, so that again we find support for the principle of independent surface action.

The molecules in adsorbed films on solutions of organic substances in water are frequently in a state of a two-dimensional gas. Oil films on water may exist as solid or liquid films. In the case of so-called expanded films (12), the heads of the molecules act as a two-dimensional gas, while the tails form a two-dimensional liquid. The molecules of oils adsorbed on solids, such as those that are responsible for some of the lubricating properties of oils, and those involved in the phenomena of flotation of ores, usually show little or no tendency to move over the surface. In other words, the molecules appear to be attached rigidly to the surface.

Many of the equations that were developed in the quantitative studies of the velocities of heterogeneous reactions assumed that bare spots on the surfaces were distributed over the surface according to statistical laws. Such statistical distribution would not occur unless the molecules possessed a certain degree of mobility over the surface, for the molecules that are removed by the reaction are those that are adjacent to holes already existing. Volmer and others have shown experimentally that adsorbed atoms frequently possess great mobility even on solid surfaces and thus act like two-dimensional gases of high viscosity.

I believe that the principle of independent surface action will be useful in studying many properties of organic substances which have hitherto been too complicated to be treated quantitatively. Within recent years I have made some attempts of this kind.

When a liquid is separated into two parts, along a surface having an area of 1 sq. cm., two new surfaces with a total area of

2 sq. cm. are formed. The surface tension or free surface energy measures the work done per unit area in forming the new surfaces. The total surface energy γ , which is equal to the free surface energy extrapolated back to the absolute zero, represents the total energy change per unit area. For all the pure hydrocarbons, such as pentane and nonane, γ is equal to about 48 ergs cm.⁻². The fact that this value is practically independent of the length of the hydrocarbon chain proves that the surface forces are very nearly uniform over the whole of the hydrocarbon molecule.

When a hydrocarbon, such as hexane, evaporates, molecules pass from the interior of the liquid into the vapor. If we consider a drop of hexane liquid to be removed from a large volume of the liquid into the free space above it, the work that would be needed to form this drop would be equal to $S\gamma$ where S is the surface area of the drop. Since we are regarding molecules as having surfaces possessing certain properties, we may say that the work necessary to remove a single molecule of hexane from the liquid, which is the latent heat of evaporation per molecule, will also be equal to $S\gamma$, where S is now the surface area of the molecule and γ is the surface energy of the molecule per unit area.

The molecular surface S for the molecule of vapor may be calculated from the molecular volumes (molecular weight divided by density), assuming the surfaces to be the same as in the case of closely packed spheres. This assumption would probably be quite accurate for large molecules, but would be only a rough approximation in the short chain hydrocarbons. From the known values of the latent heats of evaporation, the values of γ can then be calculated. Practically all of the normal hydrocarbons, with the exception of methane, give the value $\gamma = 34 \pm 1$ ergs cm.⁻². This value is of the same order of magnitude as the value 48 found from measurements of surface tension. The fact that γ is found to be constant proves that the work done in removing molecules from the liquid to the vapor phase is strictly proportional to the molecular surface. In other words, the latent heat of evaporation is proportional to the two-thirds power of the molecular volume.

This theory can readily be extended to cover the case of the

heats of evaporation of the various aliphatic alcohols. If S is the total surface of the molecule of vapor, then aS is the surface of the head of the molecule (hydroxyl group) while cS is the area of the tail (hydrocarbon chain). We may let γ_a and γ_c represent the surface energies per unit area of the heads and tails respectively when the molecule is in the vapor phase. Thus $Sa\gamma_a$ is the total energy of the head and $Sc\gamma_c$ the total energy of the tail.

If the molecules of alcohol in the liquid phase were arranged at random, that is, if they did not orientate each other appreciably, and did not tend to form clusters (segregation), then it may readily be shown that the total interfacial surface energy in the liquid between the hydroxyl groups and the hydrocarbon chains will be $Sac\gamma_{ac}$, where γ_{ac} is the interfacial surface energy per unit area. We should therefore be able to calculate the latent heat of evaporation, λ , from the difference between the energies in the vapor and liquid phases.

$$\lambda = S(a\gamma_a - ac\gamma_{ac} + c\gamma_c)$$

If we take $\gamma_a = 193$, $\gamma_c = 34$, and $\gamma_{ac} = 34$, we get excellent agreement between the observed latent heats of evaporation and the structures of most monobasic alcohols. We have already seen that γ_c is equal to 34 as the value found for the evaporation of pure hydrocarbons. The value $\gamma_{ac} = 34$ was found as a result of experiments on the vapor pressures of mixtures of alcohol and water. The interfacial energy between water and a hydrocarbon is about 59, so that the value 34 is of the right order of magnitude. The surface energy of water is 117, but this naturally represents the surface energy of the least active part of the water molecule, whereas the energy γ_a equal to 193 corresponds to the most active part of the hydroxyl group so that this value also appears reasonable.

In the case of the alcohols having very long hydrocarbon chains another effect can be clearly seen from the experimental results. In the molecule of vapor the hydroxyl group is able to bury itself at least partially among the coils of the hydrocarbon tail, so that the surface energy of the vapor molecule decreases considerably, beginning with chains of five or six carbon atoms in length.

With shorter chains than this, the hydroxyl group is probably fully exposed. Particularly interesting results which are in good agreement with the principle of independent surface action are found in the case of dibasic and tribasic alcohols. The heat of evaporation depends to a great extent on whether the separate hydroxyl groups are able to come into contact with each other in the molecule of vapor and thereby decrease the surface energy.

The theory can readily be extended to calculate the partial vapor pressures of binary solutions. The complete theory, taking into account orientation and segregation of molecules within the liquid, would be very complicated, but in many cases where the forces between molecules are not too strong, these effects can be neglected in a first approximation. Assuming then a random orientation and distribution of the molecules, the total surface energy per molecule in a solution of any given concentration in terms of interfacial surface energies, such as γ_{ac} , and surface fractions, such as a and c , the work done in transferring a molecule from a liquid to a vapor phase can then be calculated, and thus by applying the Boltzmann equation, it is possible to calculate the deviations from Raoult's law. Thus, the partial pressure of any liquid in a binary mixture is given by

$$p_A = AP_A \exp (\varphi S_A \beta^2 / kT)$$

where p_A is the partial pressure of the substance A, the total pressure of the pure component A is P_A ; the mole fraction of the component A is represented in this equation by A . The quantity S_A is the surface area per molecule of area; φ is a constant characteristic of the binary mixture but independent of the concentration of the components, which can be calculated in terms of such quantities as a , c , γ_{ac} , etc. The quantity β may be called the surface fraction of the component B in the binary mixture of A and B. It corresponds to the ordinary conception of mole fractions but is expressed in terms of the relative surfaces of the molecules instead of the numbers of the molecules. Thus

$$\beta = BS_B / (AS_A + BS_B)$$

This equation with only one adjustable constant, φ , apparently agrees in general better with experimental data than a somewhat

similar equation with two adjustable constants derived by van Laar on the basis of thermodynamical considerations.

C. P. Smyth has recently used this equation in connection with his own measures of the vapor pressures of binary mixtures. The agreement, in most cases, is fairly good, but, as is to be expected in the case of more polar molecules, mixtures of alcohols with water show considerable deviations. It is probable that these can in large part be taken into account by developing the theory further to allow for orientation and segregation of the molecules within the liquid.

Views of the type which I have been discussing may thus be applied quantitatively, often with considerable accuracy, in studying the interactions between molecules of organic substances. The energy relations based on the conception of surface forces between molecules, together with the Boltzmann equation, frequently permit decisions to be made as to the mechanism of various surface phenomena. For example, in expanded films of oils on water it has often been assumed that the molecules could remain erect on the surface without touching one another. Simple energy considerations of the kind which we have been using indicate immediately that this is impossible. The tails of the molecules must remain in contact with each other in the case of long chains, but with shorter chains, the molecules may separate but must then lie flat upon the surface of the water. The principle of independent surface action affords one of the greatest safeguards against the setting up of impossible hypotheses.

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THE CONSTITUTION AND STRUCTURE OF ULTRAMARINES¹

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The problem of the constitution and structure of ultramarine, the splendid blue paint formerly extracted from lapis lazuli, has puzzled scientists ever since Giumet, a hundred years ago, discovered a method of preparing this dye synthetically. The difficulties of getting an insight into the nature of this remarkable kind of sodium aluminium thiosilicate are manifold. The author and his collaborators attacked the problem by means of x-rays, comparing the results obtained with those for some related silicates, such as nosean and hauyne. A certain part of the constituents of the ultramarines, which are easily replaceable by other elements, do not have fixed positions within the crystalline structure, but must be considered as "errant." A certain radical containing sodium, silicon, aluminium and oxygen is common to all ultramarines, but is electrically charged like the ammonium ion and hence cannot be separated from the ultramarine in the free state. The sulfur is present as a cause of color but is predominatingly "errant," being dispersed throughout the whole crystalline mass. The results of the calculation of the relative intensities of the x-ray diffraction lines are in good agreement with the observed values.

¹ This is an abstract of a paper which has been published in full in the *Transactions of the Faraday Society* **25**, 320 (1929). This abstract is published here to complete the Symposium.

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MOLECULAR STRUCTURE AS INTERPRETED BY X-RAY DIFFRACTION MEASUREMENTS IN LIQUIDS

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The x-ray diffraction halos obtained in liquids have been known since 1916, but only during the past few years has any endeavor been made to use x-ray diffraction as a means of studying molecular structure.

It is not the purpose of this paper to give a historical account of even the recent experiments. Because of the limited space it is deemed advisable to present only the results obtained in the laboratory of the author, for by this policy a simpler and more connected account is possible, yet without giving an incorrect impression as to the present state of the subject. For the history and development of the diffraction of x-rays in liquids, Drucker's paper (1) should be consulted. In the author's first contribution (2) he adopted the theory that the molecules of the liquid are not in independent motion, and that, on the contrary, each molecule has a marked effect upon the orientation of its neighbors, particularly if the molecules are not symmetrical. There results a molecular arrangement called *cybotaxis*, which here and there throughout the liquid, proves to be sufficiently orderly to cause x-ray diffraction effects. Indeed, the liquid acts as if composed of very imperfect and small crystals of the substance. According to this view, Bragg's diffraction law, $\lambda = 2d \sin \theta/2$ should apply for the determination of the separation of the sets of the most sharply marked planes containing diffraction centers.¹ There are several reasons for believing that such an approximation to space arrangement must exist in liquids. Perhaps the simplest way of appreciating the viewpoint is to recognize that the differ-

¹ λ is the wave length of the x-rays, d the separation of planes, and θ the angle of the deviation of the ray by diffraction.

ence between a liquid and a solid is not caused by discontinuities in the laws of force applicable at molecular ranges, but by a difference in the stability of configuration. The actual force between molecules in the two cases cannot be greatly different as is witnessed by the relatively small differences in the latent heats of evaporation. But doubtless the most effective reason for the belief in the molecular space arrangement in liquids, or the cybotactic condition, is contained in the nature of the results obtained by the use of the application of Bragg's law to measurements in liquids. The discussion of the paper, however, will assume the correctness of the method.

It is to be understood that the present discussion will not include any consideration of "liquid crystals." In these the molecules are very long. It has been found that there is a space arrangement of the molecules, the long chains being parallel and hence lying in parallel planes. The "liquid crystalline" condition may be regarded as an extreme case of the phenomena discussed in this paper.

Practically all the observations of other workers have been made with the method of photography, using halos and drawing conclusions from the density of the silver of the film. In the series of experiments of the author, the Mo $K\alpha$ radiation, filtered by zirconium oxide, a slit spectrometer and an ionizing chamber are utilized. The x-rays, in passing through the liquid, are in part diffracted and the ionization chamber determines the relative intensities of the x-rays at different angles of diffraction. The monochromaticity of the radiation is very important in an attempt to attain high accuracy in the location of the diffraction peaks on the curves showing the variation of relative intensity with the angle of diffraction. For this reason it is advisable to make comparisons among observations taken with the same equipment. This is an additional reason why the results reported upon in this paper are limited to the observations in the laboratory of the author. A detailed explanation of the conclusions here presented can be found in the published articles of the author and his co-workers (3). All observations were made at room temperature excepting in a few cases where a hot air blast was used to bring the compound just above the melting point.

DIAMETERS OF STRAIGHT CHAIN MOLECULES

Measurements have been made upon primary *n*-alcohols, *n*-paraffins, and *n*-monobasic fatty acids. Figure 1 shows the nature of the experimental results for the primary *n*-alcohols. The number of carbon atoms in the molecule is indicated by the

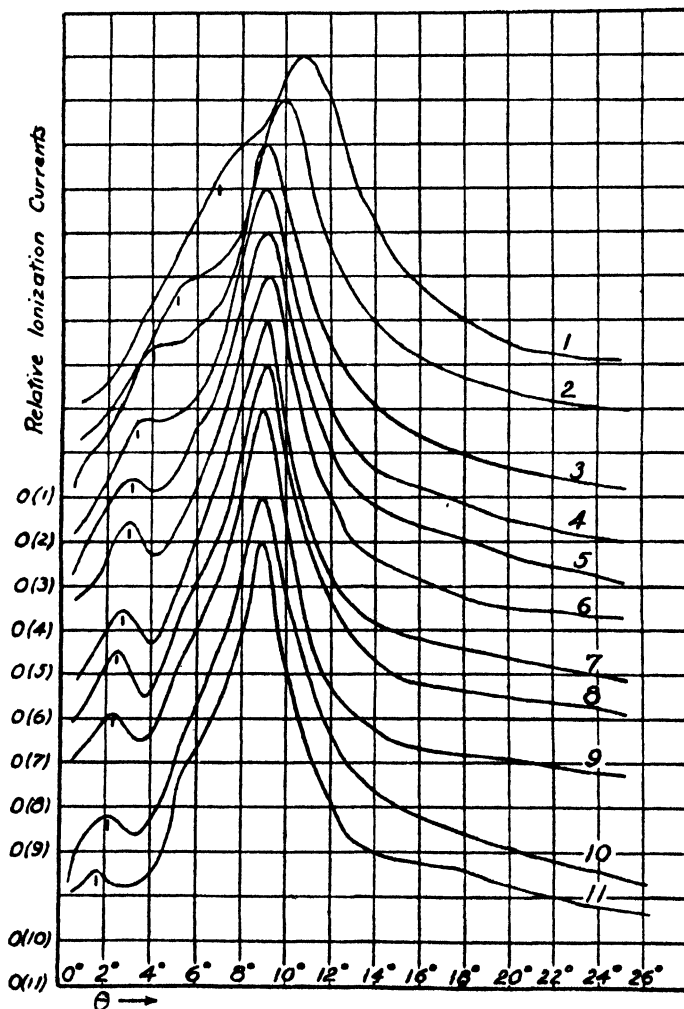


FIG. 1. THE X-RAY DIFFRACTION CURVES FOR PRIMARY *n*-ALCOHOLS CONTAINING ONE TO ELEVEN CARBON ATOMS

number of the curve, all the alcohols between methyl and lauryl alcohol being included. The curves are shifted vertically so that they may be compared on one diagram. The readings of ionization current at the peak of the curves have been made alike, so that the values are only relative for any one curve and not between curves. The interpretation is that the more prominent peaks are caused by the most marked arrangement of the molecules. With elongated molecules, such as in the alcohols, the molecular forces are certainly unsymmetrical and one may expect a molecular arrangement corresponding to this lack of symmetry. In other words, the most marked arrangement would seem to be caused by the "shape" of the molecules; and this would be a parallel arrangement of molecules. The most prominent peak would then correspond to the separation of the parallel planes in which the molecules lie and the separation of these parallel planes would be regarded as the diameter of the molecules. It is noticed that the more prominent peak of each curve of figure 1 is not at the same angle of diffraction. Using Bragg's law the various separations of planes or of molecular diameters are computed and the results for the various *n*-alcohols are shown in figure 2. (The second peak in the *n*-alcohol curves will be mentioned at a later point). In a manner similar to those with the alcohols, measurements were made on fatty acids and upon paraffins and these results are indicated in figure 2. Several interesting points are observed. (1) The diameter of the paraffin chain is independent of its length. This is but one of the numerous verifications of the correctness of the acceptance of the measurements as the diameter of the atom. (2) The *n*-alcohols and the fatty acids have diameters which are practically independent of length of chain, if the chain contains at least four or five carbon atoms. (3) The variation of the diameter with a less number of carbon atoms is what we would expect from the view that the carbon atoms do not form a straight but a staggered chain. (4) Since the diameter of a carbon atom may be regarded as approximately 1.5 Å. u., the magnitude of the diameters also leads to the conclusion that the carbon atoms are not in a straight but a zig-zag line, somewhat similar to the lines that can be drawn connecting carbon atoms in

the diamond. Any detailed discussion of their precise arrangement in these chains would exceed our experimental evidence and is omitted from this article. (5) According to figure 2, with the

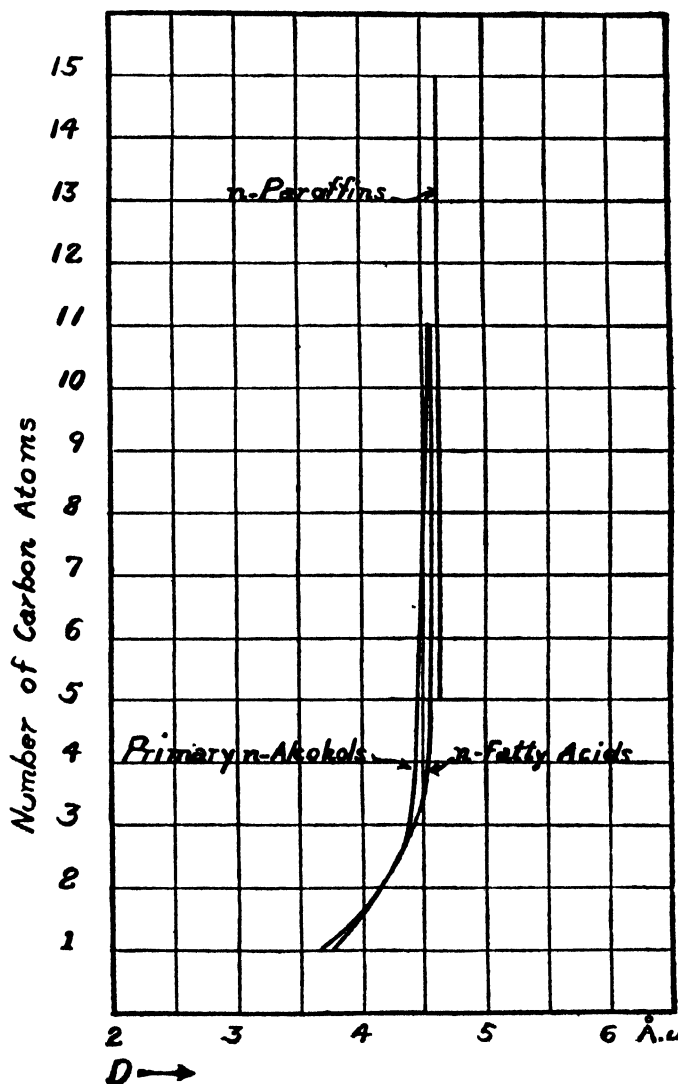


FIG. 2. THE DIAMETER OF THE MOLECULE AS DEPENDENT UPON CARBON CONTENT IN PRIMARY *n*-ALCOHOLS, *n*-MONOBASIC FATTY ACIDS AND *n*-PARAFFINS

highest content of carbon atoms, the diameters of the *n*-monobasic fatty acids and the *n*-alcohols, 4.55 Å.u., are the same to within the error of measurement. But the *n*-paraffins have a greater diameter, 4.64 Å.u. This may be ascribed, not to the differences at the ends of the chains, but rather to the difference in the rigidity of the chains. This conclusion receives further verification at a later point in the report.

In the case of the *n*-paraffins, the curves for which are not shown, there is only one important diffraction peak. Here probably the arrangement of molecules disclosed is limited to but one set of planes containing the lengths of the chains. Thus the arrangement is not very complete. The molecules lie parallel, but their positions in the direction of the length are somewhat indifferent. But the *n*-paraffins furnish a splendid opportunity for determining the length along the molecule of the space occupied by the carbon atom. It is found that, if one takes the best values of densities and computes from them the lengths of the molecules, and assumes the area occupied by the molecule is the square of the diameter, 4.64 Å.u., the following formula gives the correct value of the computed length:

$$L = 1.24 n + 2.70 \text{ (Å.u.)} \quad (1)$$

Here *n* is the number of carbon atoms and 2.70 Å.u. is allowed for the two hydrogen atoms at the ends of the molecules. The value 2.70 may be in considerable error, but the 1.24 is probably within 1 per cent of the actual value.

DOUBLE MOLECULES PRODUCED BY THE POLAR GROUPS, OH AND COOH, IN STRAIGHT CHAINS

The second and smaller peak in the *n*-alcohol diffraction curves in figure 1 shows an additional set of planes and these planes are separated by distances that are much greater than the length of one molecule and much less than the length of two molecules, if these lengths are estimated from equation (1). Moreover, these distances of separation of the planes increase linearly with the number of carbon atoms, as is shown in figure 3 where the results for both the monobasic fatty acids and *n*-alcohols are given. This

verifies the conclusion in the preceding paragraph with regard to the diameter of the molecule, for, according to that interpretation, the diameter does not vary linearly with the number of carbon atoms, whereas the length does. A careful consideration of

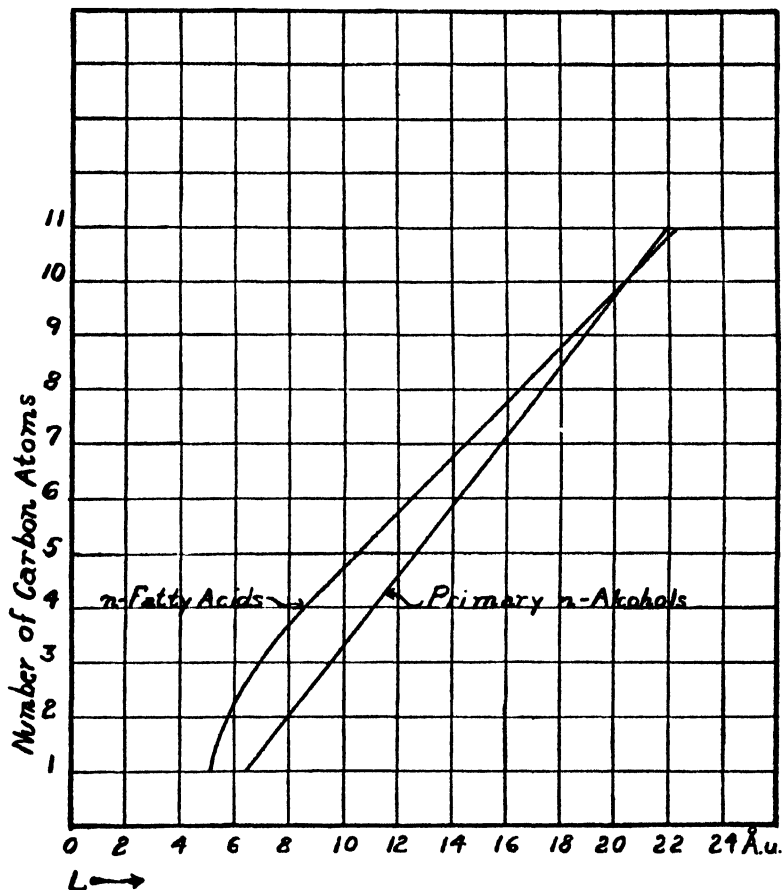


FIG. 3. SEPARATION OF PLANES (CAUSED BY LENGTH OF DOUBLE MOLECULES) AS DEPENDENT UPON NUMBER OF CARBON ATOMS

the values of the long separation of planes shows that these planes are produced by the arrangement (1) of the molecules as double molecules, two OH groups being together and the two molecules forming one straight chain, and (2) of two such double

molecules lying side by side with the two pairs of OH groups not directly adjacent, but slipped by one another so that the set of planes containing them is not normal to the length of the chain. The significant point is that the second peaks in the cases of the two series of straight chain compounds referred to, indicate double molecules with the OH (or COOH) groups together and both molecules pointing in the same line away from the pair of OH (or COOH) groups. The pairing is by a head to head and not a head to tail arrangement.

DOUBLE MOLECULES CONDITIONED ON THE POSITION OF POLAR GROUP OH IN CHAIN MOLECULES

Table 1 is a table of isomers of certain *n*-alcohols, together with the *n*-alcohols. An examination of this table will show that there are these paired or double molecules in every case where the group OH is attached to the end carbon atom or the one next to the end, but that if the OH is in a branch elsewhere, the straight chain pairing ceases. Then the length, as determined by the separation of planes, agrees closely with the estimate of the length of a single molecule made from equation (1), and the OH groups in parallel molecules lie in planes perpendicular to the molecular lengths.

Precisely the same experience is found with the isomers of *n*-octyl alcohols prepared by Professor E. Emmet Reid of Johns Hopkins. 1- and 2-Octanol give the double molecules and 3- and 4-octanol, single molecules, as shown in table 1. So far as tested by the author, the methylheptanols with the OH group in the 1 or 2 position show double molecules, whereas those with the OH group in the 3 or 4 position show single molecules. It would seem that a generalization is practically justified, namely, that the double molecules in the straight chains depend upon the attachment of the OH group to the carbon atom at the end or next to the end of the chain.

EFFECT OF BRANCHES UPON DIAMETER OF CHAIN MOLECULES

Table 2 shows the effects of an OH or a CH₃ or of the combination when placed in a branch of the straight chain molecule. It is noted that the change in diameter is not the same in all cases

TABLE 1
Double molecules as dependent upon the position of the OH group

NAME	SECOND PLANAR DISTANCE	STRUCTURE
	<i>A.u.</i>	
<i>n</i> -Amyl alcohol.....	12.6	C-C-C-C-C-OH
Isoamyl alcohol.....	12.2	C-C-C-C-OH C
<i>sec</i> -Butylcarbinol.....	11.3	C-C-C-C-OH C
<i>sec</i> -Amyl alcohol.....	11.3	C-C-C-C-C OH OH
<i>tert</i> -Amyl alcohol	8.5	C-C-C-C C OH
Diethylcarbinol.....	8.9	C-C-C-C-C OH
<i>n</i> -Hexyl alcohol.....	14.2	C-C-C-C-C-C-OH OH
Methyl- <i>n</i> -butylcarbinol.....	14.9	C-C-C-C-C-C OH
<i>n</i> -Heptyl alcohol.....	15.7	C-C-C-C-C-C-C-OH OH
Di- <i>n</i> -propylcarbinol.....	10.5	C-C-C-C-C-C-C OH
1-Octanol.....	16.8	C-C-C-C-C-C-C-C-OH OH
2-Octanol.....	14.6	C-C-C-C-C-C-C-C OH
3-Octanol.....	11.3	C-C-C-C-C-C-C-C OH
4-Octanol.....	11.7	C-C-C-C-C-C-C-C OH

for a similar branch. CH_3 in a branch increases the diameter in amyl alcohol 0.6 Å.u., in octyl alcohol 0.5 Å.u., but in heptane

TABLE 2
Increase in diameter (Å.u.) caused by branches

INCREASE			ALCOHOLS		INCREASE			
2C on different atoms	2C on same atom + 1C on another	2C on same atom	Name	Number of isomers	OH + CH_3 on same atom	CH_3	OH	OH + CH_3 on different atoms
		0.55	Butyl	1				
			Amyl	5	0.65	0.5 0.7	0.4 0.45 0.35 0.45 0.0 0.0 0.0	0.65
			Hexyl	1				
			Heptyl	2				
			Octyl	3				
			Octyl	3	0.30 0.22 0.38			
			Octyl	4				
			Octyl	9				
			π -PARAFFINS					
1.04		1.04	Heptane	8		0.61		
1.04	1.05	1.04				1.04		
	1.37	1.04	Octane	1				

from 0.6 to over 1.0 Å.u. OH in a branch increases the diameter 0.4 Å.u. in amyl, 0.35 Å.u. in hexyl, 0.45 Å.u. in heptyl and scarcely a noticeable amount in octyl alcohol. The combination

of both CH_3 and OH in branches, whether with same carbon atom or not, does not seem to give a greater increase than CH_3 alone. Other items can be found by reference to table 2. The variations may not be attributed rightly to the compounds, because the possible errors due to impurity are not fully eliminated. But the distinctly larger effect of the branches on the molecular diameter in the case of paraffins is sufficiently marked to reach the conclusion, already suggested above, that the paraffin chains do not retain their rigidity of shape. On the other hand, the alcohol molecules seem to retain their "straight" characteristic. The experience with the isomers gives increased confidence in the correctness of the method of x-ray examination.

BENZENE AND CYCLOHEXANE RINGS

The writer has examined the following derivatives of benzene and cyclohexane: benzene, toluene, *o*-, *m*- and *p*-xylene, mesitylene, ethylbenzene and isopropylbenzene; cyclohexane, methylcyclohexane, *o*-, *m*- and *p*-dimethylcyclohexane; phenol, aniline, cyclohexanol and cyclohexanone; 2-hydroxy-1, 3-dimethylbenzene and three isomers, *o*-, *m*- and *p*-toluidine, and *o*-, *m*- and *p*-cresyl methyl ether. It seems that the examination of the benzene and cyclohexane derivatives gives certain results that are obtained more directly than in the examination of crystals. For example, one is able to secure the thickness of the rings very directly because the most prominent diffraction peaks in these substances, which are caused by molecular shape, correspond to the thicknesses of these rings. That the rings are flat is attested not only by the marked asymmetry which gives these strong diffraction intensities, but also by the small alteration in the so-called thickness with substitutions. As an illustration, in table 3 are given the changes that occur in the thickness of the rings with simple substitutions. It is noted that the substitution of OH and NH_2 produces alterations which are too small to measure. Also, CH_3 , C_2H_5 , and $\text{CH}(\text{CH}_3)_2$ produce increases in thickness that are only small fractions of the diameter of the space they would occupy. The thicknesses of benzene and of cyclohexane are 4.70 and 5.10 Å.u., respectively.

If computations are made from the densities of benzene and cyclohexane and if it is assumed that, in each case, the molecules are grouped as flat disks would be piled, then the dimensions of benzene and cyclohexane rings as determined by these experiments are as shown in figure 4. The literature on crystal measurement shows that the thickness of the benzene ring is only 3 Å.u. But this value is obtained not directly from the x-ray measurements in crystals but from the arrangement in carbon atoms in the diamond and in graphite. In short, the x-ray measurements in crystals determine the dimensions of the unit cell but do not measure the thickness as directly as has been done in these liquid

TABLE 3

Increase in diameter produced by substitution. Benzene alone, 4.70 Å.u. Cyclohexane, 5.10 Å.u.

NAME	STRUCTURE	INCREASE IN DIAMETER IN Å.u.
Phenol	C_6H_5OH	0.07
Aniline	$C_6H_5NH_2$	0.05
Cyclohexanol	$C_6H_{11}OH$	-0.06
Cyclohexanone	$C_6H_{10}O$	-0.06
Toluene	$C_6H_5CH_3$	0.36
Methylcyclohexane	$C_6H_{11}CH_3$	0.25
Ethylbenzene	$C_6H_5C_2H_5$	0.29
Isopropylbenzene	$C_6H_5CH(CH_3)_2$	0.65

experiments. In view of the evidence justifying the correctness of our method, one may be confident that the thicknesses of these rings in liquids are as shown in figure 4. Here are shown also the dimensions of hexagons having areas equivalent to those computed for benzene and cyclohexane. Also the diameters of the alcohols, acids and paraffins. The comparison shows a striking equality of the latter to the diameter of the benzene ring. This would lend weight to the view of the staggered arrangement of the carbon atoms in the benzene ring, for the evidence in figure 2 and in the value 1.24 Å.u. in equation (1) is that the carbon atoms are staggered. It may also be added here that all of the tests made on the derivatives of benzene and cyclohexane indicate that the

corresponding "rings" are in each case fixed units in the structure of the molecule.

The benzene and cyclohexane rings show also the existence of polar molecules. With cyclohexanol, there is a second set of planes accounted for by the double molecules produced by the

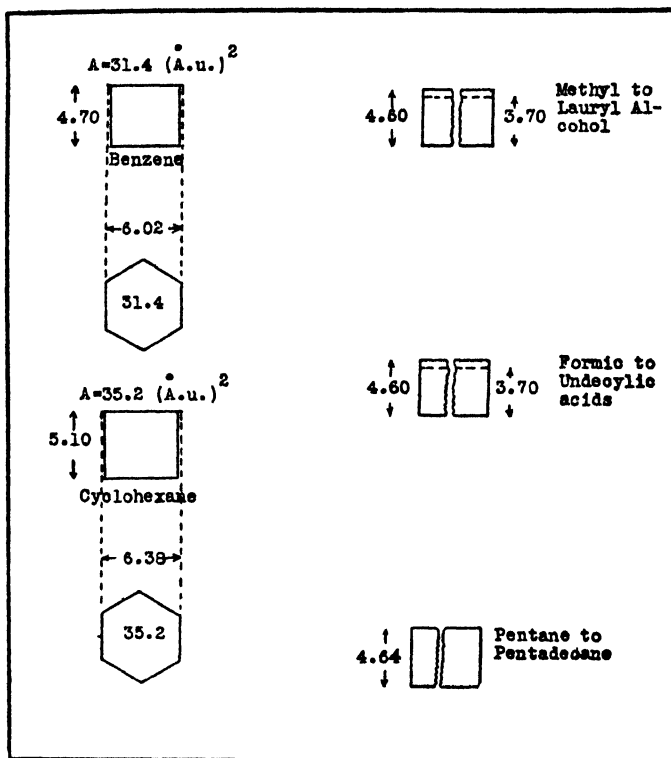


FIG. 4. COMPARISON OF THICKNESS OF BENZENE AND CYCLOHEXANE WITH DIAMETERS OF STRAIGHT CHAINS

juxtaposition of the OH groups of two of the molecules of two disks lying in a plane. Phenol shows the same characteristic. All four of the hydroxydimethylbenzenes show these double molecules, two of them, however, very faintly. In all these cases, however, the second set of planes is fairly normal to the set of planes parallel to the disks. This is known from the fact that

the distance measured between planes is, according to computations, equal to twice the length of a molecule.

The thickness of the molecule of a benzene or a cyclohexane derivative depends not only upon the substitutions but upon their location as well. Several *ortho*, *meta* and *para* derivatives were investigated and the increases in thickness over the thicknesses of the unsubstituted rings were obtained. These derivatives, with the corresponding increases in thickness stated respectively in parentheses after each one, are as follows: *o*-, *m*- and *p*-dimethylcyclohexane (0.52, 0.54, 0.39 Å.u.), *o*-, *m*- and *p*-xylene (0.81, 0.65, 0.47 Å.u.), *o*-, *m*- and *p*-toluidine (0.42, 0.37, 0.26 Å.u.), and *o*-, *m*- and *p*-cresyl methyl ether (0.80, 0.51, 0.16 Å.u.). Bearing in mind that differences more than 0.05 Å.u. are probably real, it is certain that in these four derivatives the *para* position gives the least thickness of ring. This is of course significant, but it may be too early to generalize from these four only. For example, similar observations, for the most part on other derivatives, have been made by Sogani (4), Krishnamurti (5), and Herzog and Janke (6) with the di-*n*-propylcarbinol and 2-methylhexane. In the former, the diameters clearly measure 4.85 Å.u. and 4.5 Å.u. The second value is precisely the diameter of the corresponding *n*-alcohol. This means that the di-*n*-propylcarbinol is to be regarded as a straight chain with the OH as a branch. This is further verified by the fact that the measured distance of separation of a third set of planes, 10.5 Å.u., is the length of the single molecule as computed by equation (1). The separation of planes by the length of one molecule is in accord with the previous statement that double molecules are not formed by OH unless the attachment is to the carbon atom at the end or next to the end. The other example is 2-methylhexane. This compound, which was prepared very carefully by the Ethyl Gasoline Corporation and has subsequently been tested for purity, gives two diameters, one 5.25 Å.u. and the other 4.84 Å.u. The former is .61 Å.u. greater than the diameter of *n*-heptane and the latter .20 Å.u. greater. The increase in two diameters agrees with the previous conclusion that the paraffin molecule is easily distorted. It is a significant fact that the groups of the molecules in any one case

may be so regular in structure as to enable two diameters to be measured, and, as with di-*n*-propylcarbinol, the molecular length in addition.

PURITY OF COMPOUNDS

It is obvious that x-rays can not be used to determine the nature of an impurity in a liquid, but x-rays sometimes give helpful and convincing evidence. Our first experience was with an impurity in decyl alcohol. Our observations showed that the sample contained heavy molecules. We suspected bromine. The Eastman Kodak Company kindly redistilled the decyl alcohol. Then it gave results which were in accord with those of the other *n*-alcohols. Our second experience was with *n*-pentane. This gave a diffraction peak at 8.1° , which was not the same as for the other *n*-paraffins. But upon request, the Eastman Kodak Company prepared a sample of synthetic *n*-pentane, and the peak was found at 8.8° , or exactly the position of the diffraction peaks in the other *n*-paraffins, with the exception of *n*-decane. Through the kindness of Dr. George Calingaert, we were able to secure *n*-decane synthetically prepared. Again a similar shift in the diffraction peak took place and *n*-decane gave the same diffraction peak as the other *n*-paraffins. The fourth experience was with mesitylene. It possessed a second peak, to which reference has already been made, and it was thought that this might be caused by an impurity. The Eastman Kodak Company kindly redistilled the sample, with the result that the second peak increased in relative intensity. This shows that the slight impurity actually interfered with the arrangement of the molecules producing a second set of planes.

NATURE OF A SOLUTION

The above remarks on purity are made merely to indicate the unexpected usefulness of the x-ray diffraction study of molecular structure. It is not the purpose of this paper to go beyond a discussion of molecular structure but attention might well be called also to the importance of these x-ray studies as indicating the nature of a solution. If, as it is here claimed, the liquid forms

temporary groups of molecules, then one might expect that in a solution we would have the solute participating in the molecular structure space arrangement of the solvent, as is really the case in solid solutions. So far as the experiments in our laboratory and abroad have shown, this picture indeed proves actually to occur and we have a simple conception of a solution. This view is that the solute participates in the molecular space array of the solvent. It must not be supposed, however, that this simple picture is an adequate one. The findings of x-rays from diffraction in solutions are not yet sufficiently extensive to give the varied details.

When one examines with care the evidence which is only briefly sketched in the foregoing, he can scarcely avoid being impressed with the simplicity and directness of the interpretation of the results in terms of the cybotactic condition. Moreover, he realizes that the molecular forces involved are comparable to those found in the crystalline form of the same material, and that thus both the x-ray evidence and general considerations give great confidence in the essential correctness of the theory of the cybotactic condition. As to just how temporary any given small orderly group may be, there is as yet no evidence. Doubtless the orderliness of the arrangement changes from time to time at any point. That the semi-orderly groups occupy a large part of the volume, is shown by the comparison of the intensity of diffraction with the liquid and the solid. In several cases examined, the intensity of diffraction from the liquid at a peak is approximately as large as that from the solid (the same liquid frozen) at its corresponding peak. We are dealing, therefore, not with the unusual but with the usual when we describe the liquid as containing orderly groups. With this conception, our picture of several liquid phenomena will be altered. For example, the vibrations of the molecules are not independent and the kinetic and potential energies are cared for by acoustic waves, much as in a crystal. In fact, preliminary observations show a variation with temperature much like that with crystals. The theories of liquid phenonema should now be examined with cybotaxis as a hypothesis.

The studies thus far have emphasized, by agreement with chemi-

cal beliefs, confidence in the existence of the cybotactic condition in liquids. The foregoing evidence leads to the hope that examination of liquids by means of x-rays may lead to many contributions to molecular structure as well as to liquid structure.

GENERAL CONCLUSIONS

The general conclusions that may be drawn from a study of the details of the experiments briefly reviewed above, are as follows:

1. The diameters of the straight chain molecules—*n*-alcohols, *n*-monobasic fatty acids and *n*-paraffins—are relatively as follows: 4.55, 4.55 and 4.64 Å.u., respectively.

2. The distance occupied by a carbon atom in the *n*-paraffin molecule is 1.24 Å.u., and the assumption that the same value occurs in the other two straight chain molecules leads to consistent results. The formula for the length of the *n*-paraffin molecules is

$$L = 1.24 n + 2.70 \text{ Å.u.}$$

where *n* is the number of carbon atoms and 2.70 Å.u. is the allowance for the two terminal hydrogens.

3. The terminal polar OH and COOH produce a doubling of the molecules with the polar groups adjacent to one another and the molecules forming a straight chain twice the length of one molecule. The polar group OH will cause this doubling if attached to the end carbon atom or the atom next to the end, but if in a branch elsewhere, this kind of doubling of the molecule ceases. Inasmuch as the molecules are lying side by side, the attachment of the polar group at the side instead of causing any form of doubling that can be detected by the x-rays aids and possibly increases the regularity of the arrangement of molecules in the cybotactic groups. There is no reason herein for saying that the effect of the polar group OH is less in one case than in the other. The effect is merely different.

4. The effect of branches upon the diameter of the chain molecules indicates that the *n*-alcohol chains are fairly rigid in comparison with the *n*-paraffin chains. The latter seem to bend with the attachment of a simple branch.

5. The benzene and cyclohexane molecules have a distinct flatness. The thicknesses are 4.7 and 5.1 Å.u., respectively. The areas of these molecules in a plane perpendicular to the thicknesses are, respectively 31.4 and 35.2 (Å.u.)². A polar group OH as a substituent may cause a doubling of molecules in the plane of the disks.

6. The *para* position of two substituents in benzene and cyclohexane gives the least thickness of the molecules.

7. The conception of benzene and cyclohexane molecules as having somewhat the same structure as the straight chain but forming a kind of ring, is in accordance with the x-ray measurements.

8. X-ray measurements are of some value in distinguishing between a compound and its isomer. They are also capable of detecting the presence of small quantities of heavy atoms.

9. A consideration of all these measurements leads to an increased conviction of the correctness of the view that molecules in liquids in general are in a cybotactic condition. That is, they arrange themselves into semi-orderly temporary groups. This fact is important in a consideration of the nature of a solution and many liquid phenomena.

10. There are numerous details concerning specific molecules that are shown by the experiments, but which cannot be enumerated in an abstract. For example, di-*n*-propylcarbinol is found to be a "straight" chain with the OH as a branch.

The author desires to mention his indebtedness for the data of this paper to Dr. Wm. D. Crozier and Mr. H. A. Zahl, who as research assistants have taken the necessarily large number of painstaking observations.

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BAND SPECTRA AND CHEMISTRY

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I. INTRODUCTION

The study of the spectra of individual atoms, the so-called line spectra, with the help of the quantum theory has been of the greatest value in giving us an understanding of the electronic structure and properties of atoms (1). In the last few years, the center of interest in spectroscopic investigation seems to have shifted from line spectra to the spectra of molecules, the so-called band spectra. At present most of our available information on molecular spectra has to do with diatomic molecules in the vapor state, but as time goes on we shall doubtless slowly learn more about the spectra of polyatomic molecules. The progress from atoms to diatomic molecules to polyatomic molecules is associated with a steadily increasing complexity of the corresponding spectra, and a steadily increasing difficulty in the analysis. Although from the standpoint of chemistry diatomic molecules in the vapor state constitute a very limited class, they are nevertheless molecules, and a knowledge of their structure as obtained from the analysis of band spectra and from the quantum theory can take us a long way toward a fundamental understanding of molecular structure in general.

The ways in which molecular spectra can be put to use in problems of chemical interest may be placed under the following headings: (a) We may use the presence of various bands in an absorption or emission spectrum as a means of determining the presence or concentration of various molecules. (b) By accurate measurement and quantum analysis of the spectrum of a particular kind of molecule, we can obtain knowledge of many important numerical properties of that molecule. By generalization of such results and with the help of the new

quantum mechanics, rapid progress is now being made toward the solution of the problems of valence and molecular structure. We shall now consider in turn these two uses of band spectra, the first in section II, the second in sections III-V.

II. DIAGNOSTIC USES OF BAND SPECTRA IN CHEMICAL PROBLEMS

Spectra of polyatomic molecules

A great deal of work has been done in mapping the absorption spectra of liquids, solutions, and (to a less extent) vapors of polyatomic molecules, especially of organic compounds and of inorganic compounds containing complex ions. Although comparatively very little has as yet been done, on account of their complexity, toward a detailed analysis of such spectra, their general nature from the theoretical standpoint may be said to be understood (see section IIIc below). Such spectra are of use in qualitative and quantitative analysis and in the study of chemical equilibria. They are also often useful in establishing the presence of various groups or bonds in molecules, even though very little is as yet known of the theoretical relations involved.

Spectra of diatomic molecules

Turning now to simpler molecules, we encounter a large number of band spectra, which are commonly obtained by passing electrical discharges of one kind or another, and most of which have been known for a number of years (2). Until recently the origin of most of these spectra has been in dispute. The Swan bands, for example, now definitely known to be emitted by the C_2 molecule, were by various investigators attributed to CH , C_2H_2 , etc. But the detailed application of the quantum theory has now made it possible to determine with certainty the emitters of practically all known band spectra of the diatomic type. Table 1 contains a list of some of the diatomic molecules whose band spectra are known (3) (4).

Table 1 is of interest in two ways. First, it shows the existence of a number of molecules which are not ordinarily known in chemistry, but which certainly exist as intermediate products

TABLE 1
Some molecules of which band spectra are known†

MOLECULE	OCCURRENCE OF SPECTRUM	MOLECULE	OCCURRENCE OF SPECTRUM
CH	Flames; sun*; A.H. or A.N. + C compounds	ZrO	Stars*
NH	Sun*; A.N. + C ₂ H ₂ I, etc.	PbO	Pb arc in air
OH	Flames; sun*; very hot H ₂ O vapor*; A.H.	H ₂	Geissler tubes
MgH	Sun-spots*; cooler stars*; Mg arc in H ₂	He ₂	High-current discharges in pure helium at low pressure
HgH	Hg + A.H.; Geissler tubes	C ₂	Flames; sun*; comets; A.H. or A.N. + C compounds
CaH	Sun-spots*; cooler stars*; Ca arc in H ₂	N ₂	Sparks in air; Geissler tubes; A.N.
LiH, AlH, CuH, AgH, AuH	Metal arcs in H ₂ ; also vapor of hot metal in contact with H ₂ *	N ₂ ⁺	Sparks; aurora; comets
HCl ⁺	Sparks	O ₂	Air*; electrical discharges
BO	Sun-spots*; cooler stars*; A.N. + BCl ₃ + O ₂	O ₂ ⁺	Geissler tubes
CO	Geissler tubes, etc.	S ₂	Geissler tubes; vapor*
CO ⁺	Comets; Geissler tubes, etc.	Cl ₂	Geissler tubes; vapor*
CN	C arc in air; sun*; hot-tish stars*; comets; A.N. + C compounds	I ₂	Geissler tubes; vapor*; and recombination of I atoms
CS	Geissler tubes, etc.	ICl	Vapor*
NO	Cu and other arcs in air; sparks in air; A.N. + O compounds; NO gas*	Na ₂	Vapor*
AlO	Al arc in air	NaK	Vapor*
SiO	Si arc in air; C + SiO ₂ vapor	K ₂	Vapor*
SiN	A.N. + SiCl ₄	MgF, CaF	Fluorides in carbon arc
MgO	Burning Mg	CaCl, MgBr, SrI, etc.	Excess of alkaline earth metal in presence of halogens*
CuO	Cu arc in air	CuF, CuCl, CuBr, CuI	Vapor of Cu ₂ Cl ₂ , CuCl ₂ , etc. (* or in A.N.)
TiO	Sun-spots*; cooler stars*; Ti arc in air	SnCl	Discharge in SnCl ₄ ; A.N. + SnCl ₄
		AgCl, AgBr, AgI	Vapor*
		AuCl	A.N. + AuCl ₃

† This list is not exhaustive in respect either to molecules or to occurrence of spectra. The spectra given occur as emission spectra, except as indicated by an asterisk (*), which denotes absorption spectra. The abbreviations A.H. and A.N. denote active hydrogen and active nitrogen respectively.

in chemical reactions, or as equilibrium products at high temperatures; and second, it shows where such molecules are found. For example, band spectra show the existence of large numbers of the diatomic molecules CH, OH, and C₂ in ordinary flames, the CH and C₂ molecules respectively being responsible for the bluish and greenish colors of such flames. In a similar way, the presence of CO⁺, CN, and N₂⁺ molecules in the tails of comets is demonstrated, as well as the presence of various molecules in the sun and stars. Again, band spectra have shown that the vapors of the alkali metals are not strictly monatomic, as had long been supposed, but contain considerable percentages of diatomic molecules, and that in mixed alkali metal vapors, mixed molecules occur. A study of the OH absorption band spectrum in highly heated water vapor (5) has disclosed the importance of OH, hitherto neglected, in the equilibrium of H₂ and O₂. Likewise, the high intensity of the CN bands in the carbon arc burning in air, and in the sun, indicates that the equilibrium of carbon and nitrogen at high temperatures favors this molecule (6). Chemical reactions occurring in active nitrogen are a source of many interesting band spectra disclosing various intermediate reaction products. For example, when any hydrocarbon vapor is introduced into active nitrogen, the CN, C₂, and CH bands appear; certain compounds such as C₂H₅I give also the NH bands (7); oxygen-containing molecules give NO spectra, and so on.

III. BAND SPECTRA, ENERGY LEVELS, AND MOLECULAR PROPERTIES

a. Introduction

There are two basic rules, first proposed by Bohr and since established by many experiments, which are essential in line and band spectra. These are (a) the energy of an atom or molecule is capable of taking on only a discrete set of values, corresponding to a set of so-called energy levels, and (b) whenever the molecule gains or loses energy in the form of light, the quantity of energy gained or lost is proportional to the frequency of vibration ν of the light waves: $h\nu = E' - E''$ (E' and E'' are the energy values for two energy levels out of the dis-

crete set which the molecule possesses; E' is by definition greater than E'' ; h is Planck's constant).

In the study of the spectrum of an atom or molecule, one first obtains a knowledge of the wave-lengths and their relative intensities. This knowledge in itself has many useful applications, but it is less fundamental than the knowledge of energy levels (and their quantum numbers) which can be obtained from it. For when one knows the energy levels E of a molecule, one can compute all possible spectrum frequencies from the relation $h\nu = E' - E''$. A precise knowledge of the energy levels also has many important applications to problems of reaction mechanisms and of chemical equilibria. But we can go farther: from the numerical values of the energy levels, and their spectroscopic behavior, we can get various other important numerical data about the molecule (moments of inertia, vibration frequencies, angular momentum of electrons and of nuclei, law of force acting between the atoms, etc.), and can obtain a great deal of insight into its physical and chemical behavior. This we can do not merely for its lowest or normal state of energy, but also for its various excited or activated states.

In the next section (III*b*) we shall consider the main features of the energy level diagram for a diatomic molecule in the vapor state. In section III*c* we consider briefly the various types of molecular spectra for diatomic and polyatomic molecules, keeping in view their relation to chemical problems. Section III*d* contains a discussion of the energy levels of some actual molecules (H_2 , O_2 , I_2 , NO). The object of this section is to give some idea, by means of examples, of the numerical magnitudes involved and of the varied kinds of information which can be obtained from a study of the energy levels.

b. Energy levels of diatomic vapor molecules; general relations (8)

For a diatomic molecule we have energy of the electrons, energy of vibration of the nuclei along the line joining them, and energy of rotation of the nuclei about their center of gravity. All of these are capable of taking on only discrete values, so long as the molecule remains undissociated. The energy levels of a

diatomic molecule are accordingly subject to a threefold classification, each level being characterized by three kinds of quantum numbers. One group of quantum numbers specifies the condition or configuration of the electrons, a vibrational quantum number (n) determines the amplitude of vibration, and a rotational quantum number (K) fixes the rate of rotation.

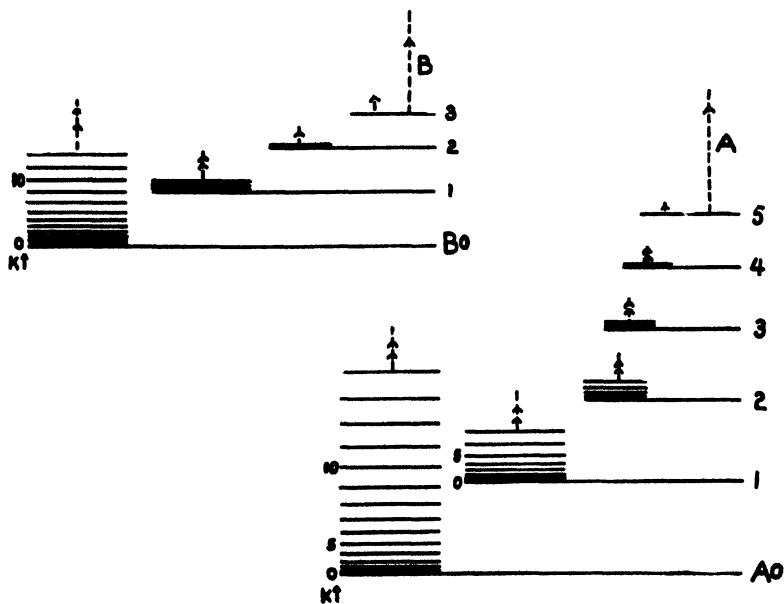


FIG. 1. SCHEMATIC ENERGY LEVEL DIAGRAM FOR DIATOMIC MOLECULE

The diagram shows two electron levels (A and B), each with a set of vibrational levels (A_0, A_1, \dots , and B_0, B_1, \dots), and each vibrational level having a set of rotational levels. The spacings are qualitatively correct, but the quantitative spacing of the rotational levels is relatively much too large.

Figure 1 is a qualitatively correct, but quantitatively impossible, diagram of energy levels for a diatomic molecule. In the figure, the ordinates represent energy, commonly measured from the lowest level as zero, while the abscissas have no significance. Two "electron levels," A and B , are shown, with each of which is associated a family of vibrational levels; the vibrational quantum numbers (n) are given on the right (A_0, A_1, A_2, \dots ; B_0, B_1, B_2, \dots). The amplitude of vibration is

a minimum (not quite zero, see section IIIId, p. 517) for $n = 0$, and increases with n . It will be noted that the vibrational levels (a) are more closely spaced than the electron levels, as can for example be seen by comparing the energy interval between A0 and A1 with the interval A0 to B0 (this relation is usually but not always true in practice); (b) differ in spacing for different electron levels (here A and B); (c) decrease, slowly, in spacing as n increases (in figure 1 the rate of decrease of spacing has been exaggerated). Now for every vibrational level there is a family of rotational levels, characterized by different values of the rotational quantum number K . The rotational levels show the following characteristics: (a) they are much more closely spaced than the electron or vibrational levels (in practice, their relative spacing is always much smaller than in figure 1); (b) they differ in spacing for different electron levels and, to a lesser extent, for different vibrational levels; (c) their spacing increases with K , approximately in proportion to K^2 . In figure 1, only a part of the vibrational and rotational levels is shown; the existence of the others is indicated by arrows.

The impressions given by figure 1 will be clarified in section IIIId by a discussion of the energy levels of some actual molecules (figures 2-5).

The effect of liquefaction or solidification on the energy levels of a diatomic gas, and the energy levels of polyatomic molecules are discussed in section IIIc.

c. Energy levels and band spectra (8)

Absorption and emission spectra; origin, classification, and structure. In the space available, it is not possible to discuss how one can determine energy levels and quantum numbers from an analysis of band spectra, but a brief description can be given of the various types of band spectra and their relation to molecular energy levels.

In an emission spectrum line, a molecule which has by some means been excited to a more or less high energy level makes a quantum jump to one of its lower energy levels, giving out the corresponding energy in the form of light. In an absorption

spectrum line, a molecule, ordinarily starting from one of the lower rotational levels of its lowest vibrational and electronic state (thermal equilibrium near room temperature), is carried by the absorption of a light quantum to a higher energy level. Resonance and fluorescence spectra are emission spectra of molecules which have been excited by light absorption. Chemiluminescence spectra are emission spectra of molecules which have been excited in the course of a chemical reaction. Raman spectra will be discussed below.

Molecular spectra can also be divided into three classes according to the type of energy change in the molecule: (a) pure rotation band spectra, (b) oscillation-rotation band spectra, (c) electronic band spectra. In pure rotation bands, the molecule goes from one rotational energy level to another, without any change in its vibrational or electronic state (for example, from $K = 4$ to $K = 5$ of the level A_0 in figure 1). Since the spacing of the rotational energy levels of a molecule is always comparatively small (see figure 1), and since the rotational quantum number never changes by more than one unit, the energy changes and so the frequencies involved in such spectra are very small, so that they lie exclusively in the far infra-red. In vibration-rotation bands, the molecule goes from one vibrational and rotational level to another, but without any change in its electronic state (for example, from $K = 3$ of level A_0 to $K = 2$ of A_1 in figure 1). The frequency here is approximately proportional to the interval between two vibrational levels, since the rotational quantum number changes only by 0 or ± 1 units, which represents only a very small energy change. Since, furthermore, the vibrational quantum number rarely changes by more than one or two units in vibration-rotation bands, the corresponding frequencies are rather small and such spectra lie almost exclusively in the near infra-red. In electronic bands, the molecule undergoes a change in its electronic state as well as in its vibrational and rotational states. Since electronic energy levels are in general widely spaced, electronic bands generally correspond to large energy changes and large frequencies and lie in the visible or ultra-violet part of the spectrum; but infra-red

electronic bands are also possible. In electronic band spectra, the rotational quantum number never changes by more than one unit, but the vibrational quantum number may change by large amounts.

The fact that rotational quantum numbers never change by more than one unit as a result of light absorption is important, in a negative sense, for photochemical theory, since it shows that light can rarely, if ever, seriously influence chemical reactions through its effect on the state of rotation of a molecule. Also important is the fact that the vibrational quantum number practically never (i.e. with only a very small probability) changes by more than one or two units as a result of the absorption of infra-red wave-lengths, unless they belong to an electronic band spectrum. Thus, absorption of infra-red light corresponding to the pure rotation or rotation-vibration spectrum of a molecule can hardly be expected to have much effect on its chemical activity, unless perchance the molecule is already on the verge of instability. But the absorption of wave-lengths (usually ultra-violet) belonging to an electronic band spectrum can—but need not necessarily—profoundly influence the activity of a molecule, either directly by producing an alteration in the electronic structure, or indirectly by setting the molecule into a violent state of vibration which in many cases goes so far as direct dissociation (see section IV below).

The foregoing remarks should hold for polyatomic as well as for diatomic molecule spectra, although the systems of rotational and especially of vibrational and electronic levels are more complicated and more closely spaced in the former case, because of the greater number of degrees of freedom.

In structure, the spectra of all the types mentioned above, for polyatomic as well as diatomic molecules, consist in general of a great number of sharply defined wave-lengths, but in those electronic band-systems¹ where dissociation of a molecule results

¹ A band system is a set of bands all of which correspond to the same electron jump, i.e., in an absorption spectrum, to the same electron configuration in the activated state. A complete band spectrum consists of a number of band-systems.

from light absorption (or conversely, where association is accompanied by light emission), part or all of the spectrum is continuous.

Raman spectra. Raman spectra are emission spectra of a type somewhat related to fluorescence spectra (9); a light quantum of frequency ν_1 (say, from a mercury lamp) strikes a molecule and bounces off with a somewhat smaller frequency ν_2 , the energy $h(\nu_1 - \nu_2)$ being imparted to the molecule, taking it to a higher energy level. Or sometimes ν_2 is somewhat greater than ν_1 , the energy $h(\nu_2 - \nu_1)$ being abstracted from the molecule. Raman spectra, although their position in the scale of wavelengths is mainly determined by the exciting frequency ν_1 , may be classified under the same three headings as ordinary band spectra—pure rotation, oscillation-rotation, and electronic Raman spectra—according to the nature of the energy change in the molecule.

The rules which govern the possible energy level changes in a molecule in Raman spectra are very different from those for ordinary band spectra; in fact, it is the rule that changes which could not occur at all in ordinary processes of light emission or absorption are the usual changes with Raman spectra (9). For example, the rotational quantum number generally changes by 0 or ± 2 in Raman spectra where it would usually change by ± 1 with ordinary spectra. Again, changes in the rotational and vibrational quantum numbers without change in the electronic state are possible in Raman spectra for homopolar diatomic molecules (i.e. molecules like H_2 and O_2 , composed of two equal atoms), whereas in ordinary emission and absorption spectra such molecules have only electronic bands.² Similarly, in the pure rotation and oscillation-rotation spectra of polyatomic molecules, changes commonly occur, in Raman spectra, in quantum numbers which never change in the case of ordinary emission or absorption bands. These various peculiarities make

² Of the diatomic molecules, only those which have an electric moment (heteropolar molecules) are capable of absorbing or emitting pure rotation and vibration-rotation bands as well as electronic bands. Homopolar molecules have only electronic bands.

the Raman effect very valuable as a means of supplementing the information which we can obtain about molecular energy levels from infra-red absorption spectra; just those facts which are withheld from us by the latter are disclosed by the Raman spectra.

Liquids, solids, and polyatomic molecules. It is of interest to consider how the energy levels of a diatomic molecule are altered when the vapor is condensed to form a liquid or solid. In the case of liquid H_2 , we know from band spectrum evidence (Raman effect) that the rotational and vibrational energy levels are practically the same as in the gas (10), and from other evidence that they persist even in the solid state (11). In the case of other non-polar molecules, (N_2 , O_2 , CO) the vibrational levels are practically the same in liquid and vapor (presumably also in the solid), but the rotational levels are probably destroyed (11) and replaced by some sort of a continuous energy distribution, so that the corresponding band spectra must consist of diffuse bands, instead of being composed of sharp lines like those of the vapor. It is probably safe to say that the electron levels of non-polar molecules are practically the same in position in the solid or liquid as in the vapor. Of course if the liquid contains molecular species not present in the vapor, as O_4 is probably present (12) in liquid O_2 , these may give new spectra. Also, spectra which are weak in the gas may become relatively strong in the liquid. For polar molecules (e.g. HCl) the changes in the energy levels on condensation are doubtless more radical than for non-polar molecules, especially in cases where the liquid is ionized or the solid is an ionic lattice (e.g. $NaCl$).

In gases at very high pressure, the rotational energy levels tend, as in liquids, to be obliterated, because of the frequency of collisions. All band spectra become more diffuse as the pressure is increased.

The absorption spectra of many organic molecules have been studied in both liquid and vapor states, especially by Henri and his students. The spectra are in general very nearly the same in the two cases, except for a greater diffuseness of the bands in the liquids, indicating that the rotational levels which are present in the vapor molecule are suppressed in the liquid.

Our knowledge, based on band spectra, of the structure and properties of polyatomic molecules is at the present time less than that of diatomic molecules, in spite of the large amount of empirical spectroscopic material on the former. The reason for this lies in the complexity of the energy levels and spectra of polyatomic molecules. In such spectra, the band lines in ordinary electronic bands are usually too numerous and too closely packed to be properly measured with the usual instruments; and even if a complete set of measurements were at hand for such a spectrum, the task of analysis and interpretation would be likely to be exceedingly difficult. A beginning has, however, been made in the work of Henri and Schou on formaldehyde vapor (13). Much progress has also been made in infra-red absorption bands of the vibration-rotation type where, although the complexity and the difficulties of interpretation are still formidable, they are much less than for the electronic bands. In the future a study of such infra-red bands, in conjunction with Raman effect data, will probably lead to a great deal of information about the normal states of the simpler polyatomic molecules. But it will probably be some time before we begin to obtain such a large amount of detailed information from the band spectra of polyatomic molecules as we have been getting from those of diatomic molecules. A good understanding, from a study of band spectra, of the higher (activated) electron states of polyatomic molecules, important especially for photochemical and electron-impact reactions, will probably come about especially slowly, since it depends on the interpretation of the very complicated (visible and ultra-violet) electronic band spectra. It may be that by the time this is possible, the mathematical technique of the new quantum mechanics will have developed to such an extent that it will be easier to determine what we want to know about polyatomic molecules by pure calculation.

d. Energy levels of H_2 , N_2 , O_2 , NO , and their interpretation

Electron levels. Keeping in mind the general scheme of figure 1, let us now examine the arrangement of the energy levels of some familiar molecules as revealed by band spectra, and see

what we can learn from them. In figure 2 are plotted the best known electron levels of the molecules H_2 , O_2 , and I_2 (4) (14). Each plotted level is of course only the lowest of a whole family of levels corresponding to a variety of states of vibration and of rotation of the molecule, i.e., the levels shown here are those one would get if the energy of vibration and rotation of the nuclei were omitted from consideration. On the right is a scale of calories per mol, on the left a scale of absolute temperatures such that RT is equal to the number of calories given on the right. This gives a rough idea of the temperatures needed to excite the molecules to the various levels. The horizontal dotted line for each molecule indicates the dissociation energy (in the case of oxygen, there is an uncertainty of about $\pm 13,000$ calories).^{*} From the positions of these lines one can see at once that it is possible for a molecule to have temporarily, stored up in its electron configuration, much more energy than would suffice to dissociate it. Such highly energized molecules are, however, capable of dissociating under certain conditions, such as collisions with other molecules, or (see below) often spontaneously. An H_2 molecule in its lowest excited electron level has, in fact, enough energy to dissociate both itself and another H_2 molecule if they should collide. We do not yet know whether this particular process actually occurs in nature, but we do have evidence that molecules which have been excited from their normal state to higher electron levels are chemically very reactive. (For the meaning of the symbols $^3\Sigma$, $^1\Sigma$, $^1\Pi$, etc. in figure 2, see section V, p. 532.)

Returning to the H_2 molecule, it is of interest to consider what may happen to an excited molecule if it does not collide with another molecule, or if it escapes intact from one or more such collisions, as is not unlikely. If it is in one of the excited states

^{*} The heat of dissociation will be accurately known from band spectrum data as soon as we know the energy X required to excite the O atom from its normal (1P) state to its low 1D state. The heat of dissociation is $163,000 - X$ calories. X probably lies between 25,000 and 50,000 calories; in figure 2 the value $X = 36,000$ has been assumed. See Herzberg, G.: *Z. physik. Chem.* **4B**, 1223 (1929).

$^1\Sigma(B)$ or $^1\Pi(C)$ of figure 2, we know that it must almost certainly, after a short time, make a quantum jump to the normal state of H_2 , giving out its excess energy as a quantum of short wave-length ultra-violet light ($h\nu = E' - E''$). If it is the lowest state marked, $^3\Sigma$, it very probably makes another kind of

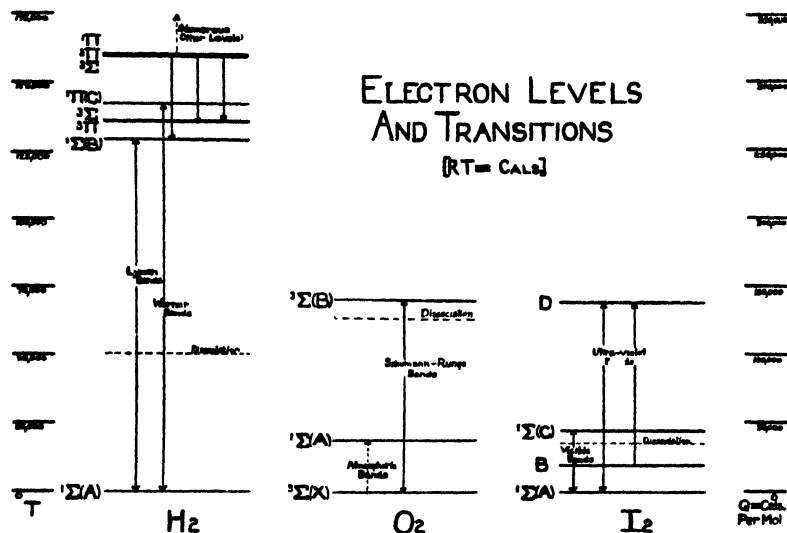


FIG. 2. MOST IMPORTANT KNOWN ELECTRON LEVELS (FULL HORIZONTAL LINES), AND DISSOCIATION ENERGY (DOTTED HORIZONTAL LINES), OF H_2 , O_2 , and I_2

(See reference (4), where additional excited levels of H_2 will be found. The existence of the B level of I_2 is not certain.) The designations of the levels are partly empirical and without general significance (A , B , C , D , X) and partly systematic ($^1\Sigma$, $^3\Sigma$, $^1\Pi$, etc.); for the significance of the latter, see Part V below. The important band spectra corresponding to transitions between these levels are shown by vertical lines; arrow heads at the top of the lines indicate spectra which are known as absorption spectra; arrow heads at the bottom indicate known emission spectra. The energy scale is given on the right in calories per mol (Q), on the left in terms of absolute temperature (T), in such a way that $RT = Q$.

quantum jump; while, as it were, jumping towards a certain very unstable lower $^3\Sigma$ state not shown on the diagram (this is the $1s\sigma 2p\sigma$, $^3\Sigma$ state discussed in section V, p. 532), it spontaneously dissociates into atoms, which fly apart at high speed (15). In the process (a variable) part of the energy appears as light of a frequency equal to $1/h$ times the original energy minus the energy of dissociation and the kinetic energy of the retreating

atoms.⁴ The whole process is of interest as an example of a unimolecular reaction whose mechanism is understood. This and analogous processes are also of interest from the fact that they yield the chemically active atomic hydrogen.

The reader may wonder at this point how the H_2 molecule originally got up into the excited levels just under discussion. This may have happened in various ways, as by bombardment with fast electrons or with α particles, or by collision with excited or fast-moving or ionized atoms or molecules, or by absorption of short wave-length ultra-violet light. If the activation is produced by light, the subsequent chemical reactions of the activated molecules would be classed as photochemical. The problem of reaction mechanisms will be further discussed in section IV.

Vibrational levels. Returning now to the energy level diagrams of the three molecules, we see in figure 3 the lowest portion of the diagram of figure 2 on a larger scale (14). This time we have not merely the electron levels, but also, and principally, some of the associated vibrational levels. Figure 3 makes clear how greatly the spacings of the energy levels depend on the molecular weight. The equation which describes the vibrational energy levels of any molecule is

$$E^v = (n + \frac{1}{2})h c \omega_e - (n + \frac{1}{2})^2 h c x \omega_e + \dots \quad (1)$$

In this equation the first term is the principal one, and in it $c\omega_e$ is the frequency of vibration, which is, generally speaking, greater the smaller the molecule and the lighter its atoms; n is the quantum number of vibration, whose lowest value is zero. For $T = 0$ all molecules would be in the lowest vibrational state ($n = 0$). But since the energy is given by $(n + \frac{1}{2})h c \omega_e$, there is still a residual vibrational energy $\frac{1}{2}h c \omega_e$ when $n = 0$; this may be called the zero-point vibrational energy. The existence of this energy is demanded by the new quantum theory and is shown experimentally by a study of the isotope effect in band spectra.

⁴ This, aided by other similar processes, is very probably the origin of the well-known and useful continuous band spectrum which is obtained by passing a suitable electrical discharge through hydrogen gas at low pressures.

One of the most interesting results of band spectrum analysis has been the recent discovery (16) of the existence of oxygen isotopes of atomic weights 17 and 18, in respective amounts about 1/10,000 and 1/1250 that of O^{16} . The spectrum in which the oxygen isotopes have been found is the system known as the atmospheric absorption bands, which corresponds to a transition

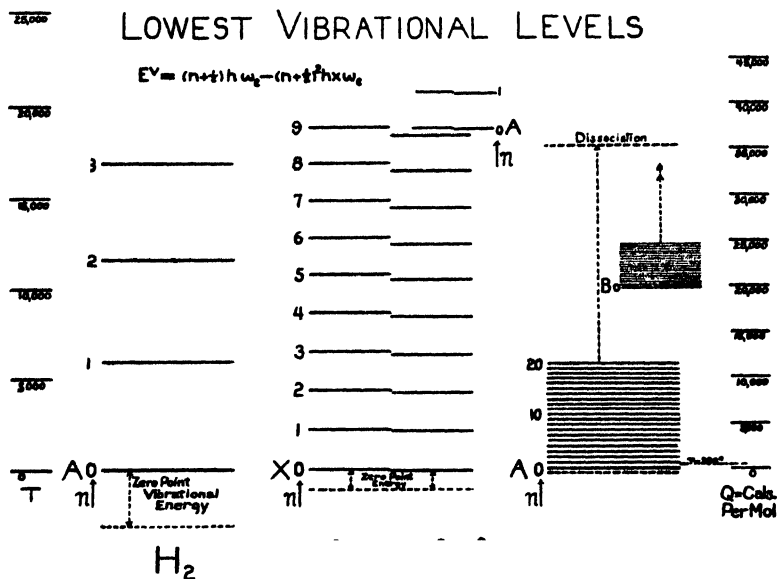


FIG. 3. LOWEST VIBRATIONAL LEVELS OF H_2 , O_2 , AND I_2

The Q and T scales are related as in figure 2. The energy is called zero for $n = 0$, although when $n = 0$ there is still some vibrational energy ("zero-point energy") which, however, cannot be removed; the dotted horizontal lines at the bottom of the diagrams show the amount of this zero-point energy. The O_2 diagram is not quite in agreement with the convention of zero energy for $n = 0$, but instead, in order more clearly to bring out the difference between the isotopes, has been drawn in accordance with the convention that the isotopes would have equal energy if the zero-point energy could be removed.

between the electron levels X and A of figures 2 and 3. These bands appear as Fraunhofer lines at the red end of the solar spectrum, being absorbed out of the sunlight in its passage through the earth's atmosphere. The very strong (O^{16}) $_2$ bands are accompanied by very faint bands slightly displaced in precisely the way predicted by the theory for $O^{16}O^{17}$ and $O^{16}O^{18}$.

There should also be other bands due to $(\text{O}^{17})_2$, $\text{O}^{17}\text{O}^{18}$ and $(\text{O}^{18})_2$, but these are surely too faint to be observed. Another interesting result of band spectrum analysis is the discovery of the carbon isotope C^{13} in the C_2 , CN, and CO bands (17).

The vibrational levels of $(\text{O}^{16})_2$ and $\text{O}^{16}\text{O}^{18}$ are shown in figure 3. So far only the levels (X0 and A0) with $n = 0$, and the level A1, are known for $\text{O}^{16}\text{O}^{18}$. The positions of the $\text{O}^{16}\text{O}^{18}$ levels shown in figure 3 have been calculated from those of $(\text{O}^{16})_2$, as can be done exactly by means of the quantum theory. The observed interval between the levels X0 and A0 differs for $(\text{O}^{16})_2$ and $\text{O}^{16}\text{O}^{18}$ by exactly the theoretical amount; the result gives a confirmation of the predicted zero-point energy of $(\frac{1}{2})h\omega_e$ ⁵. The observed interval X0 to A1 also differs for the two isotopes by exactly the theoretical amount.

Accurate measurements on band spectra offer a possibility of very accurate determinations of the atomic weights of C^{13} with reference to C^{12} and of O^{17} and O^{18} with reference to O^{16} .

Returning now to an examination of the spacing of the vibrational levels in figure 3, it is easy to see why in the cases of H_2 and O_2 the vibrational energy does not contribute at ordinary temperatures to the specific heat, since for ordinary temperatures the level $n = 1$ lies far above the quantity $RT/2$ which, for the vibrational degree of freedom, represents the equipartition value of the energy per mol. In the case of I_2 , however, the spacing of the levels is so small that the energy of the level $n = 1$ is approximately equal at room temperature to $RT/2$. Hence in I_2 there is a vibrational specific heat, the molecules being distributed at room temperature over several vibrational levels in such a way as to give an average vibrational energy of approximately $RT/2$ (in excess of the zero-point energy).

Rotational levels. We turn now to figure 4, which shows on a still larger scale the lowest energy levels of our three molecules.

⁵ The isotope effect here does not give a direct test of the presence of the energy $(\frac{1}{2})h\omega_e$ for the X0 and A0 states individually, but only shows that the difference between the values of this quantity for the X and A states (which is due to the fact that ω_e is different for the X and A states) differs in the calculated way for the two isotopes.

This time we see the rotational levels, which in figures 2 and 3 were omitted. On the scale used, the vibrational level $n = 1$ would come far above the top of the present diagram in the cases of H_2 and O_2 , but in the case of I_2 , where the vibrational levels are relatively close together, $n = 1$ appears in the figure. The rotational levels of the three molecules show the

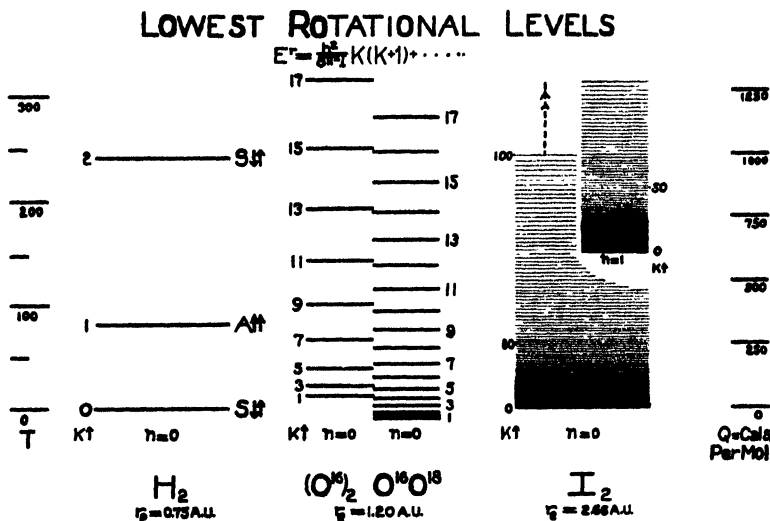


FIG. 4. LOWEST ROTATIONAL LEVELS OF LOWEST ELECTRON LEVEL OF H_2 , O_2 , I_2 .

In the case of I_2 , the lowest of the rotational levels are too closely spaced to be shown separately on the scale used. The Q and T scales are related as in figures 2 and 3. The energy is called zero for $K = 0$ in each case, except that in the O_2 diagram, the same convention has been adopted as in figure 3. The values of the equilibrium distance between the nuclei (r_e) are given in Angstrom units ($1 \text{ A.U.} = 10^{-8} \text{ cm.}$). In the case of H_2 , the symmetric and antisymmetric levels are labelled S and A , respectively, and the arrangement of the proton spins (parallel $\uparrow\uparrow$, or antiparallel $\uparrow\downarrow$) is indicated.

same sort of differences in scale as the vibrational levels. The rotational energy is given by formulas of the type

$$E' = (h^2/8\pi^2 I)K(K+1) + \dots \quad (2)$$

where I is the moment of inertia and K is the rotational quantum number. I is much larger for I_2 than for H_2 , both because of the larger mass and because of the larger equilibrium distance r_e , between its nuclei ($r_e = 0.75 \times 10^{-8} \text{ cm.}$ for H_2 and $2.66 \times$

10^{-8} cm. for I_2). This distance is known from the spacing of the rotational levels, from which (see equation (2)) I can be calculated, and so r_e , since the masses of the nuclei are known. (For a molecule composed of equal atoms each of mass M , $I = Mr_e^2/2$.)

The spacing of the rotational levels is important in connection with the rotational specific heats. In the cases of I_2 and O_2 the spacing of the levels is small enough so that the rotational specific heat has nearly the ordinary equipartition value R except at the very lowest temperatures. (Since the rotational energy of a diatomic molecule corresponds to two degrees of freedom, its equipartition value per mol is RT , which gives a specific heat R per mol.) But in the case of H_2 the spacing is quite large, so that below about $200^\circ K$. the rotational specific heat falls rapidly, and becomes practically zero at $50^\circ K$.

A number of other facts can be learned from a careful study of the rotational levels, or rather, of the band spectra from which these levels are determined. Thus a study of the hydrogen band spectra shows that in each band, alternate band lines have intensities differing in a ratio of about 3:1. The interpretation is that half the rotational levels, namely, in the case of the lowest electron level, those with odd values of K , have a statistical weight or *a priori* probability three times as great as for the even levels. (For the even levels, the statistical weight is $2K + 1$.) The explanation of this peculiarity, and of analogous relations in other homopolar molecules, is found in a combination of two factors, namely, the fact that the molecule is composed of two like atoms, and the fact that the nuclei, or protons in the case of H_2 , have an internal angular momentum.

The effect of the first factor, i.e. symmetry, alone, can be seen in the case of the rotational levels of $(O^{16})_2$. Here every other level is completely missing. Only the so-called antisymmetric rotational levels, namely those with odd values of K , are present in the case of the normal electron state. This is explained by the postulate, closely related to the Pauli exclusion principle for atoms, that in homopolar molecules only antisymmetrical states exist. To explain the difference between H_2 and O_2 , we

suppose that in $(\text{O}^{16})_2$, the O^{16} nuclei have no internal angular momentum, but that in H_2 each proton has a unit of spin. These proton spins are then able to arrange themselves in H_2 in such a way as to make possible all values of the rotational quantum number. (In $(\text{O}^{16})_2$, although each nucleus contains numerous protons and electrons, each presumably with a spin, these are evidently so arranged as to neutralize one another.) In the normal state of H_2 the antisymmetric rotational levels ($K = 1, 3, 5, \dots$) are present just as in $(\text{O}^{16})_2$; for these levels, the proton spins are arranged symmetrically, i.e. roughly speaking parallel (see figure 4), and do not affect the symmetry of the molecule as a whole. The symmetric rotational levels ($K = 0, 2, 4, \dots$) are, however, also present; this is made possible by an antisymmetrical, i.e. an antiparallel, arrangement of the proton spins (see figure 4), which makes the state of the molecule as a whole antisymmetrical, hence permitted. But the odd levels now have three times as great a statistical weight as the even levels, because a parallel orientation of the proton spins has three times as great a weight as an antiparallel orientation.⁶

There is another very curious and interesting fact about these odd and even levels in hydrogen, namely that it is extremely difficult to reverse the orientation of the proton spins, even in collisions, so that hydrogen behaves almost like a mixture of two different gases, or isotopes. At high temperatures we should expect about one-fourth of the molecules to be distributed among the symmetric states ($K = 0, 2, 4, \dots$) and about three-fourths among the antisymmetric states ($K = 1, 3, 5, \dots$). If now we cool the gas to a low temperature, all the symmetric molecules accumulate in the level $K = 0$, and the antisymmetric molecules in the level $K = 1$. Only in the course of long periods of time, in gas at atmospheric pressure, can one expect the final equilibrium to be established in which all molecules are in the state $K = 0$, because of the resistance of the proton spins to having their orientation reversed. Equilibrium is, however, rapidly

⁶ The explanation just given is too brief to be accurate. For a detailed review of the subject, see Mulliken's paper given at the September 1929 meeting of the Faraday Society.

established by the catalytic action of cocoanut charcoal at the temperature of liquid hydrogen (18). The slowness of attainment of equilibrium under ordinary conditions serves to explain some of the anomalous behavior of the specific heat of hydrogen at low temperatures (18) (19).

Relations similar to those in H_2 and O_2 have been found in other homopolar molecules. The ratio of statistical weights of alternate levels is in some cases (He_2 , C_2) 1:0 as in O_2 , in others (F_2) it is 3:1 as in H_2 , while in others it has other values. In each case, this ratio enables us to determine the internal angular momentum of the nucleus; this turns out to have a variety of values in different atoms (20).

Turning now to oxygen, the considerable differences in spacing of the energy levels of $(O^{16})_2$ and $O^{16}O^{18}$ are of interest. These differences are verified experimentally in the atmospheric oxygen bands. There is also the very striking difference that in $O^{16}O^{18}$ all the rotational levels are present, and without any alternation in statistical weight. This is exactly as expected, because the difference in mass of the two atoms in O^{16} and O^{18} is enough to destroy the symmetry which exists in the case of $(O^{16})_2$. An analogous phenomenon is found in the case of Cl_2 when the rotational levels of $(Cl^{35})_2$ and $Cl^{35}Cl^{37}$ are compared.

There are other facts about the oxygen molecule which can be deduced from its rotational energy levels. One of these is that its normal electronic state is a $^3\Sigma$ (triplet sigma) state, i.e. a state in which the electron spins give a resultant angular momentum $h/2\pi$, but in which the average orbital angular momentum of the electrons is zero. The triplet character is shown by the fact that each rotational level is a close group of three. This is not shown in figure 4, but it is very important, since it accounts for the fact that O_2 is paramagnetic. As Van Vleck has shown (21), the observed paramagnetic susceptibility corresponds exactly to that of a $^3\Sigma$ state. The triplet character of the levels is important in that it multiplies the statistical weight by three, giving the weight $3(2K + 1)$ for each K value which is present. The existence of a triplet normal level is also of interest in that it shows, according to London's theory of valence, which is mainly

a translation of Lewis' theory into quantum theory terms (see section V) that each O atom in O_2 is exerting only one of its valences; in other words, that the bond between the O atoms is a single and not a double bond. The existence of paramagnetism here and elsewhere is directly connected with the existence

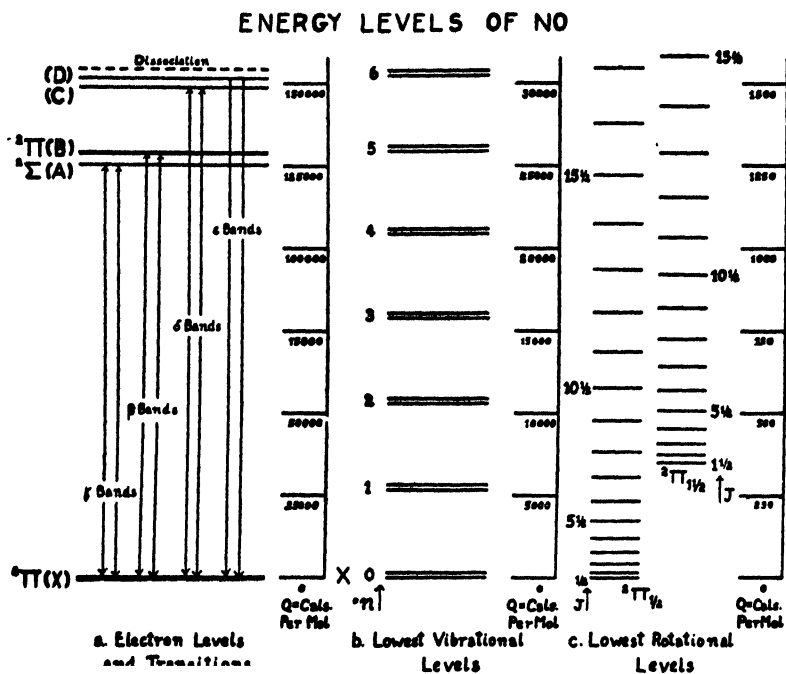


FIG. 5. ENERGY LEVELS OF NO

Figure 5a is analogous to figure 2, figure 5b to figure 3, and figure 5c to figure 4. In figure 5a the $^2\Pi$ electron levels appear as very narrow doublets; in figure 5b the $X^2\Pi$ level appears as a wider doublet (because of the larger scale), which is repeated for each vibrational level; in figure 5c the two sets of rotational levels corresponding to the two components ($^2\Pi_{1/2}$ and $^2\Pi_{3/2}$) of the $X^2\Pi$ electron level for $n = 0$ are shown.

of unsatisfied valence, although this does not imply that valence forces are magnetic in character. The paramagnetism is rather a symptom than a driving force in valence.

Energy levels of NO (example of $^2\Pi$ state). The normal electron states of H_2 , O_2 , and I_2 are all Σ levels, i.e. levels for which the average orbital angular momentum of the electrons is zero.

The rotational levels associated with such electron levels are of a particularly simple type, especially when they are $^1\Sigma$ levels, as in H_2 and I_2 . It will be of interest to consider briefly a molecule whose normal state is of a different type. The paramagnetic molecule NO, whose energy levels are well known from band spectra, has a $^2\Pi$ normal state. Figures 5a, 5b, and 5c show, in the same manner as figures 2, 3, and 4 for H_2 , O_2 , and I_2 , the electron levels, the lowest vibrational levels, and the lowest rotational levels for NO. The $^2\Pi$ normal electron state consists of two sub-states, $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$, of which $^2\Pi_{1/2}$ is slightly lower. Each of these electron sub-states has a complete set of vibrational and rotational levels (see figures 5b, 5c). The spacing of the vibrational levels is about fifteen times as great as the interval between the $^2\Pi_{1/2}$ and the $^2\Pi_{3/2}$ levels, so that the vibrational level diagram appears as a series of narrow doublets (figure 5b). In $^2\Pi$ states, every rotational level, in both the $^2\Pi_{1/2}$ and the $^2\Pi_{3/2}$ set, has a statistical weight $2(2J + 1)$, where J is the rotational quantum number (this differs from K of figure 4 in the fact that it includes the electron spin) (22). The $^2\Pi_{1/2}$ levels are non-magnetic or nearly so for small values of J , while the $^2\Pi_{3/2}$ levels are paramagnetic. At room temperature, many molecules exist in both sets of levels, so the gas as a whole is paramagnetic; Van Vleck has shown (21) that the observed paramagnetic susceptibility at room temperature is in excellent agreement with that calculated from the band spectrum data by means of the quantum theory. At low temperatures, however, the paramagnetism decreases (23), and should finally disappear with the crowding of the molecules into the lowest levels of the $^2\Pi_{1/2}$ set. The specific heat of NO should also show interesting peculiarities on account of the double electron level (24).

Band spectra and entropy of gases. From a knowledge of the energy levels of a molecule and of their statistical weights, as determined from band spectra, it is possible to calculate not only the specific heat of the gas, but also (making use of the Sackur-Tetrode equation) its absolute entropy. Giauque and Wiebe have made such entropy calculations for HCl, HBr, HI, and O_2 , and have compared the results with those obtained from

direct calorimetric measurements, assuming the correctness of the third law of thermodynamics. In all cases, the agreement is excellent. Giauque and Wiebe (25) conclude that calculations based on spectroscopic data are to be preferred to those based on calorimetric data. Corrections must, however, be made for deviations of the gas from the state of an ideal gas.

IV. BAND SPECTRA AND THE MECHANISM OF CHEMICAL REACTIONS

The most important types of homogeneous chemical reactions (26) for the present discussion are perhaps as follows:

1. Reactions produced by electron impact or by the absorption of light. It is well known that the effect of electrons of given energy is similar to that of light quanta of corresponding energy ($h\nu$), except that the conditions which the electrons must fulfil are less rigorous than those for light quanta. To produce a definite change in a molecule, a light quantum must have exactly the right frequency, while an electron can accomplish the same effect even if its energy is considerably more than the exact amount needed. Another difference is that there are no such rigorous selection rules governing electron impact as there are for light absorption; nevertheless it is true in a general way that processes which are impossible or improbable (i.e. infrequent) in the case of light absorption are also improbable for electron impact. In reactions produced by light or electron impact, the initial effect is always the activation, ionization, or dissociation of a molecule as a result, direct or indirect, of a disturbance of its electron configuration. (As already noted in section IIIc, absorption of infra-red light corresponding to pure rotation or vibration-rotation spectra is not likely to produce photochemical action.)

2. Reactions produced by collisions of the second kind, in which energy of excitation or ionization is transferred from one excited atom or molecule to another (examples: $\text{Hg}' + \text{H}_2 \rightarrow \text{Hg} + 2\text{H}$; $\text{N}_2' + \text{Hg} \rightarrow \text{N}_2 + \text{Hg}'(?)$; $\text{Ne}^+ + \text{CO} \rightarrow \text{CO}^+ + \text{Ne}$).

3. Reactions produced by the impact of fast moving atoms or molecules. These include thermal reactions. Here one may often expect large changes in vibrational and rotational energy

as a result of collisions; or sometimes rearrangements of the atoms in a complex molecule; or also often, as above, changes in the electron configuration.

A knowledge of the energy levels of a molecule, such as can be derived from band spectrum data, is obviously of value in understanding reactions of any of the above types, but we shall consider here mainly reactions produced by light absorption or electron impact.

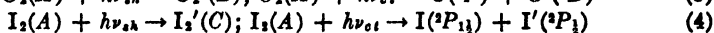
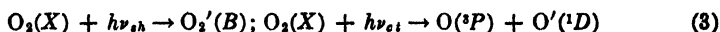
The first step in a photochemical reaction is a change in the electron state of a reacting molecule as a result of the absorption of light, nearly always of visible or ultra-violet light. There are then two possibilities: either (a) the activated molecule may dissociate spontaneously, the dissociation products thereafter often reacting further, or (b) the activated molecule may remain unchanged until, on collision with another molecule, it reacts, or until, if collision is too long delayed, it makes a quantum jump to a lower energy level, giving out radiation (fluorescence). The same possibilities exist in the case of electron impact.

The most general type of band-system¹ in the spectrum of a diatomic molecule consists of two parts; the one composed of numerous bands generally made up of sharp lines and corresponding to the transfer of the molecule from one quantum state to another, the other a continuous region of wave-lengths corresponding, in an absorption spectrum, to the transfer of the molecule from one of its lower energy levels directly to a state of dissociation, the latter being unquantized. This last process may be considered as caused by an unusually large change in vibrational energy. Such changes occur whenever, roughly speaking, the activated electron state is much less stable than the unactivated state. The theory of these phenomena was first developed by Franck (27). In many band-systems (or in most band-systems, in diatomic molecules), one finds with measurable intensity either the separate bands only, or the continuous region only. In some band-systems, however, as for example the Schumann bands of O_2 and the visible absorption bands of I_2 , and pretty generally in polyatomic molecules, both regions are strong. In such cases, a determination of the value of the

frequency for the boundary between the two regions makes possible an accurate spectroscopic measurement of the heat of dissociation, provided one knows in what electron states the dissociation products are. In cases where only the continuous region is present, an upper limit for the heat of dissociation can often be set, while in cases where only the separate bands are present, the heat of dissociation can very often be estimated fairly accurately by extrapolation (27).

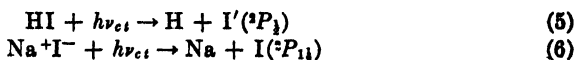
In many, especially polyatomic, molecules the part of any band-system which consists of separate bands must be further differentiated. It has been noted, especially by Henri (28), that many absorption spectra contain a region of bands composed of sharp lines, and another region (usually at shorter wave-lengths) in which the bands, while still individually distinguishable, are diffuse. In the latter case, according to Henri, the activated molecule is in a "state of predissociation," in which the rotational motions are no longer sharply quantized. The explanation of this lack of sharp quantization is probably that the activated molecule makes, after an extremely short interval (of the order of 10^{-11} sec.), a quantum jump in which it dissociates spontaneously without the emission of light (29) (30). For all practical purposes this is the same as if the dissociation had occurred simultaneously with the absorption, as in the case of the true continuous region of the band-system. Theoretically, however, the two cases are quite different. Intermediate stages between simple activation and predissociation apparently often exist, as would be expected theoretically.

The following equations represent known or probable examples of the various types of photochemical activation and dissociation. In these equations the subscripts "*ct*," "*df*," and "*sh*" in ν_{ct} , ν_{df} , and ν_{sh} refer to the type of band spectrum (continuous, diffuse, or sharp-line) which produces the given reaction. The symbols X , A , B , C , etc. refer to certain electron states of O_2 and I_2 which appear in figure 2. When no symbol is given for the initial state, the normal state is usually meant.



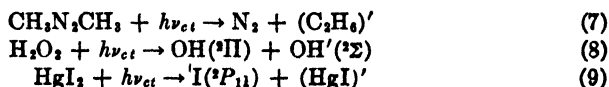
Following photochemical activation according to equation (3), ozone is formed; this probably occurs both for the sharp-line and for the continuous absorption; apparently either O_2' molecules or O atoms are capable of forming O_3 as a result of collision with unexcited O_2 molecules. In the case of I_2 (and similarly for the other halogens), photochemical action results mainly, if not entirely, from the formation of dissociated atoms.

In the cases of the alkali and hydrogen halides, only the continuous parts of the absorption band-system appear under ordinary conditions. For example (31) (32),

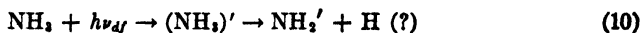


Bonhoeffer and Farkas (31) have shown that equation (5) holds probably not only for gaseous HI, but also in the case of solid HI.

Also, probably (33) (34) (35)



In the case of NH_3 there is a predissociation spectrum (29):



The examples given are among those which have been most carefully studied; large numbers of analogous cases undoubtedly exist. In connection with the above equations it should be remarked that the indicated dissociation products usually are those for the absorption region of longest wave-length in the spectrum. In general the absorption spectrum consists of a number of regions, each of which produces dissociation products in different excited states, or sometimes different dissociation products.

In addition to the two types of photochemical dissociation discussed above, a third type is conceivable; namely, one in which the activated molecule makes a quantum jump in which it dissociates spontaneously (after a time of the order of 10^{-8} sec.) *with light emission*. An example of this (15), except for the fact that the activation was produced by electron impact,

The electron state of a diatomic molecule (41) (42) is described as in the following two examples. The first of these is the formula for the normal state of the molecules N_2 , CO , and NO^+ , all of which have fourteen electrons like the Si atom. The second is the corresponding formula for the normal state of NO . The third is that for the normal state of O_2 .⁷

$$N_2, CO, NO^+: 1s\sigma^2 2p\sigma^2 2s\sigma^2 3p\sigma^2 2p\pi^4 3s\sigma^2, {}^1\Sigma \quad (20)$$

$$NO: 1s\sigma^2 2p\sigma^2 2s\sigma^2 3p\sigma^2 2p\pi^4 3s\sigma^2 3p\pi, {}^2\Pi_1 \quad (21)$$

$$O_2: 1s\sigma^2 2p\sigma^2 2s\sigma^2 3p\sigma^2 2p\pi^4 3s\sigma^2 3p\pi^2, {}^3\Sigma \quad (22)$$

The configuration formula means that the molecule contains two $1s\sigma$ electrons ($1s\sigma^2$), two $2p\sigma$, two $2s\sigma$, two $3p\sigma$, four $2p\pi$, and two $3s\sigma$ electrons, and (in NO and O_2) one or two $3p\pi$ electrons⁷ (42). The number and the first letter have essentially the same significance as for an atom, while the second (Greek) letter gives the value of a quantum number λ which does not exist for the atom, ($\sigma, \pi, \delta, \dots$ mean $\lambda = 0, 1, 2, \dots$). (Instead of the symbol λ , the symbols i_{lr} and σ_{lr} have hitherto been usual.) In the term formula ${}^1\Sigma$ or ${}^2\Pi_1$ or ${}^3\Sigma$, the Greek letter gives the value of a quantum number Λ ($\Sigma, \Pi, \Delta, \dots$ mean $\Lambda = 0, 1, 2, \dots$) which is, here and in general, equal to the sum of the individual λ 's, some of the latter taken with a positive and some with a negative sign; the superscript on the left gives the multiplicity M and implicitly the resultant spin S ($M = 2S + 1$) just as for an atom. (Instead of the symbols $\Sigma, \Pi, \Delta, \dots$ the symbols S, P, D, \dots have until recently been commonly used, although the meaning of these symbols is quite different from that of S, P, D, \dots in atoms; instead of Λ, i_l or σ_k or σ_l has hitherto been usual.) The meaning of the quantum number λ is as follows: when an atomic electron orbit with azimuthal quantum number l is placed in an electric field of suitable strength, or when the atom is replaced by a diatomic molecule, a new quantum number λ comes into existence; this corresponds to the projection of l on the electric axis (in the molecule, this axis is the line

⁷ It should be emphasized that the exact electron configurations given here for various molecules (equations (20), (21), and (22), table 2, etc.) may be subject to correction. But this possible uncertainty does not involve any essential doubt as to the principles involved.

joining the nuclei); λ is capable of taking on the integral values from l to 0, e.g. any p electron orbit ($l = 1$) gives the two cases $\lambda = 0$ ($p\sigma$ orbit) and $\lambda = 1$ ($p\pi$ orbit), while an s electron ($l = 0$) gives only the one case $\lambda = 0$ ($s\sigma$ orbit).

If one compares the electron configurations given above for Si and N_2 , it will be evident that the latter is the same as the former except for some changes in the relative order of binding of different orbits and the subdivision of the group of six $2p$ electrons in Si into two $2p\sigma$ and four $2p\pi$ electrons in N_2 ; also, the $3p$ electrons of Si are $3p\sigma$ electrons in N_2 . In a molecule, $\lambda h/2\pi$ is, for any electron, the component of electronic orbital angular momentum around the electric axis, while $\Lambda h/2\pi$ is the total angular momentum of this kind for the molecule as a whole (41) (42).

In Bohr's theory of the periodic system of the atoms (40), the idea of closed shells of electrons is of the utmost importance. The existence of closed shells depends on the empirical fact that there is a limit to the number of electrons which can simultaneously occupy the same kind of orbit (Pauli principle). Two s electrons with the same value of n make a closed shell (e.g. $1s^2$ or $2s^2$ or $3s^2$), likewise six equivalent p electrons (e.g. $2p^6$), or ten equivalent d electrons, and so on. An important peculiarity of every closed shell is that the motions of the electrons are so ordered that it has a resultant orbital angular momentum L of zero, also a resultant spin momentum S , of zero. In the case of the spins, this results from a pairing off of all the spins, each pair containing the spins of two electrons with their spin axes antiparallel (\rightleftharpoons). Since every closed shell has $L = 0$ and $S = 0$, the resultant L and S of an atom, (hence the term type, as 1P_0 in the normal state of Si), are determined exclusively by those electrons—usually the outermost ones—which are not in closed shells. In the Si atom, these are the two $3p$ electrons.

The resultant spin S , as we shall see later, is important in chemistry because $2S$ is the value V of the non-polar valence according to the theory of London and Heitler. This number $2S$ is merely the number of individual spins which are not paired off, and which have their axes parallel. (Each individual spin

has the quantum number $s = \frac{1}{2}$. Spins always set themselves with their axes either parallel or antiparallel. Two antiparallel spins give $S = 0$. Two parallel spins give $S = 1$; three, $S = 1\frac{1}{2}$; and so on. Hence $2S$ is the number of spins whose axes are parallel.) Electrons whose spins are parallel are available for valence purposes, while those whose spins are paired off with their axes antiparallel are not so available.

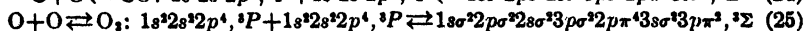
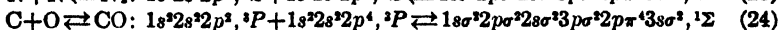
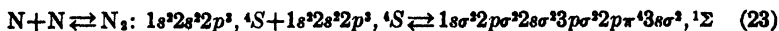
In predicting the electron configuration of the normal state of an atom, Bohr used the following structure principle ("Aufbauprinzip"). To the completely ionized atom, electrons are supposed to be added one by one, each electron being allowed to drop to the lowest available orbit; by "lowest orbit" is meant the orbit of lowest energy—the most firmly bound orbit. As successive electrons are added, successive shells become filled. The completed atom in its normal state ordinarily consists entirely of closed shells except for zero or more of the last-added electrons; these outermost electrons determine the term-type (see preceding paragraph). If one knows the relative strengths of binding of the different orbits, one can thus specify the electron configuration and (with the help of certain additional considerations) the term-type for any atom in its normal state. For light atoms the order of binding is $1s, 2s, 2p, 3s, 3p, 4s, 4p, 3d, \dots$; for heavier atoms it is $1s, 2s, 2p, 3s, 3p, 3d, 4s, 4p, 5s, 5p, 4d, \dots$ and so on. The shift in the relative strengths of binding of the $3d$ and other orbits with increasing atomic number, and analogous phenomena for heavier atoms, have important consequences for the periodic table and the properties of atoms (40).

In diatomic molecules (42), as in atoms, there are closed shells. One may also seek to set up a structure principle for determining the normal states of molecules, although the relations are more complicated than for atoms. In the first place, the closed shells are more numerous: the atomic closed shells have to be subdivided to obtain those of the molecule, as we have already seen in comparing Si and N_2 . Two σ electrons of any one kind ($1s\sigma^2, 2p\sigma^2, 2s\sigma^2$, etc.), or four π , or δ , electrons of any one kind (e.g., $2p\pi^4$, or $3d\pi^4$, or $3d\delta^4$) constitute a closed shell for a di-

atomic molecule. Such a closed shell has the value zero for the total electronic orbital angular momentum ($\Delta h/2\pi$) around the electric axis, and also has a zero resultant spin ($Sh/2\pi$). In the normal state of N_2 , CO, NO^+ , all the electrons are in closed shells, hence $\Lambda = 0$, $S = 0$ for the molecule as a whole. In the second place, the order of binding of the different closed shells varies not only with the atomic numbers of the atoms, but also with the equilibrium distance between the nuclei, and furthermore depends on the degree of disparity between the charges on the two nuclei. There is, however, a fairly definite order of binding if one limits oneself to any group of molecules which are reasonably similar in respect to the position of their atoms in the periodic table (e.g., C_2 , CN, CO, N_2 , NO, O_2). The order of binding which is probably typical for the first fourteen to sixteen electrons in such molecules is that which appears in equations (20), (21), and (22). The fact that the three molecules, N_2 , CO, and NO^+ , have the same type of normal state is an example of the truth of the statement that the order of binding of electrons is fairly definite within a group of similar molecules. The fact that the normal state of NO is obtained from that of NO^+ merely by adding one more electron in a higher orbit, without disturbing those already present, is a further example of the applicability of the structure principle in molecules.

Electron states of molecules and their atomic dissociation products

A consideration of the relationship between the electron state of a molecule and those of its component atoms on dissociation (42) raises interesting questions. It is known, for example, from band spectrum data, that CO or N_2 or O_2 in their normal states, if their vibrational energy were steadily increased up to the point of dissociation, would give two normal atoms ($C + O$ or $N + N$ or $O + O$). This dissociation and the converse process of formation of a normal molecule from two atoms can be formulated as follows:



It is evident that in the formation of such molecules, radical changes, other than merely the assignment of λ values, are required in the quantum numbers of the atomic electrons. Thus, in $N + N$ or $C + O$ one has four $1s$, four $2s$, and six $2p$ electrons, while in N_2 or CO one has two $1s$ (i.e., $1s\sigma$), two $2s$, six $2p$ (two $2p\sigma$ and four $2p\pi$), two $3s$, and two $3p\sigma$ electrons. Thus some of the atomic electrons are promoted in the formation of the molecule, i.e. their principal quantum number n is increased, while l is often also changed. If it were not for this promotion, there would be in the molecule too many $1s$ and $2s$ electrons, namely four of each, whereas only two of each are permitted according to the Pauli principle. The way in which promotion is possible is made clear only by the new quantum mechanics (42). The relations between the atomic electrons and the corresponding molecular electrons are further discussed below.

Valence theory

Equations (23) to (25) illustrate an important relation which is general: in the formation of the normal state of a stable molecule from the corresponding atoms, the multiplicity M and the resultant spin S of the molecule ($M = 2S + 1$) usually assume a low value, ordinarily the lowest possible value. This comes about through a (\rightleftharpoons) pairing off (see p. 533) of spins originally unpaired and belonging to electrons in the separate atoms. Thus in the case $N + N \rightarrow N_2$, we have in each 4S nitrogen atom three unpaired spins ($M = 4$, hence $S = 1\frac{1}{2}$, for each atom, corresponding to three individual spins, $s = \frac{1}{2}$, all parallel, hence unpaired). These evidently belong to the $2p$ electrons, since the $1s$ and $2s$ electrons are in closed shells (see equation (23)). But in the resulting N_2 molecule (${}^1\Sigma$ state, $M = 1$, $S = 0$) all the electrons are in closed shells and the six originally unpaired electron spins are all paired off.

In general, when two atoms a and b with respective spins S_a and S_b unite, the possible values of the spin S_{ab} for the molecule (if we choose the designations a and b so that $S_a \geq S_b$) are $S_a + S_b$, $S_a + S_b - 1$, \dots $S_a - S_b$. In the case of $N + N$

just discussed, we have $S_a = S_b = 1\frac{1}{2}$, giving 3, 2, 1, and 0 as possible values of S_{ab} , of which actually we find $S_{ab} = 0$ for the normal state of N_2 . According to the valence theory of London and Heitler (43), the valence V of any atom (or molecule) is equal to the number $2S$ ($= M - 1$) of unpaired spins,

$$V = 2S = M - 1 \quad (26)$$

while the number B of valence bonds established in the formation of a molecule from two atoms (or molecules) a and b is equal to the number of spin-pairs formed in this union. Evidently

$$2B = 2S_a + 2S_b - 2S_{ab}, \text{ or, } B = (M_a + M_b - M_{ab} - 1)/2 = (V_a + V_b - M_{ab} + 1)/2 \quad (27)$$

If two atoms with equal valence unite ($V_a = 2S_a = M_a - 1$, $= V_b = 2S_b = M_b - 1$), the maximum possible number of valence bonds is given by $B_{max} = V_a = V_b$. Other possibilities are given by $B = 0, 1, \dots V_a$, but the most stable state of the molecule is usually, at least when the atoms are in S states, that in which B has its maximum possible value. Thus for two normal (4S) N atoms, we have $V_a = V_b = 3$, and in the normal N_2 molecule we have $B = 3$. Similarly in the case of $C + O$ (both in 3P states) we have $M_a = M_b = 3$ and $V_a = V_b = 2$, while in the resulting normal state of CO we have $B = 2$ (see equation (24)). But (see equation (25)) in the case of two normal oxygen atoms (both 3P), with $V_a = V_b = 2$, we get an O_2 molecule whose normal state is a $^3\Sigma$ state ($M_{ab} = 3$), showing according to equation (27) that only one of the two valences of each atom has been saturated, i.e. $B = 1$ (single bond) instead of the possible value 2. When two atoms with unequal valences V_a and V_b unite, then if $V_a > V_b$, the maximum value of B is equal to V_b , and the molecule has still $V_a - V_b$ unsaturated valences. London and Heitler's valence theory applies also to polyatomic molecules, but since there is as yet little or no information for such molecules from band spectrum data and bearing on valence theory, we shall not consider them here.

According to London and Heitler's theory, the heat of dissociation of a non-polar diatomic molecule in a given state is usually greater the larger the number of valence bonds involved in its

formation. (Examples, normal states of CO and N₂; exception, normal O₂). As a result of this, it often happens that the normal state of such a molecule gives on dissociation one excited and one normal atom, instead of two normal atoms, in cases where the excited atom has a larger V than the same atom in its normal state. A good example of this is found in the case of the CN molecule (44). For this we know, from band spectra, three electron levels. These are given, together with their probable³ dissociation products, in table 2.⁷ The lowest state

TABLE 2
States of CN and of C + N

C ATOM		N ATOM		CN MOLECULE	
State	Energy	State	Energy	State	Energy*
	<i>calc.</i>		<i>calc.</i>		<i>calc.</i>
$1s^2 2s^2 2p^2, ^4S$	+37,000	$1s^2 2s^2 2p^2, ^4S$	0	$1s\sigma^2 2p\sigma^2 2s\sigma^2 3p\sigma^2 2p\pi^4$ $3s\sigma, ^1\Sigma$	-186,000
$1s^2 2s^2 2p^2, ^3P$	0	4S	0	$1s\sigma^2 2p\sigma^2 2s\sigma^2 3p\sigma^2 2p\pi^3$ $3s\sigma^2, ^2\Pi$	-145,000
3P	0	4S	0	$1s\sigma^2 2p\sigma^2 2s\sigma^2 3p\sigma^2 2p\pi^4$ $3s\sigma^2, ^2\Sigma$	-113,000

* The energy values (calories) are only approximate; they are measured from the normal state of C + N (C, 3P and N, 4S) as zero. The electron configurations given for the various states of the CN molecule are not yet entirely certain (in particular, it may be that $3s\sigma$ and $3p\sigma$ should be interchanged).

of CN is formed by the union of a normal (4S) nitrogen atom ($V = 3$) and an excited (5S) carbon atom ($V = 4$). Three valence bonds are formed ($B = 3$), leaving one free valence so that the CN molecule in its chemical behavior resembles a Cl atom, which also has $V = 1$. In the formation of the normal state of CN from C(5S) + N(4S), about 223,000 calories are given out per mol of CN; after deducting about 37,000 calories as the energy per mol required to excite C atoms from their 3P normal state to their 5S state, we still have 186,000 calories as the net energy of formation of normal CN from two normal atoms by this method.

³ The correlation between atomic and molecular states given in table 2 and elsewhere is very probable, but not absolutely certain

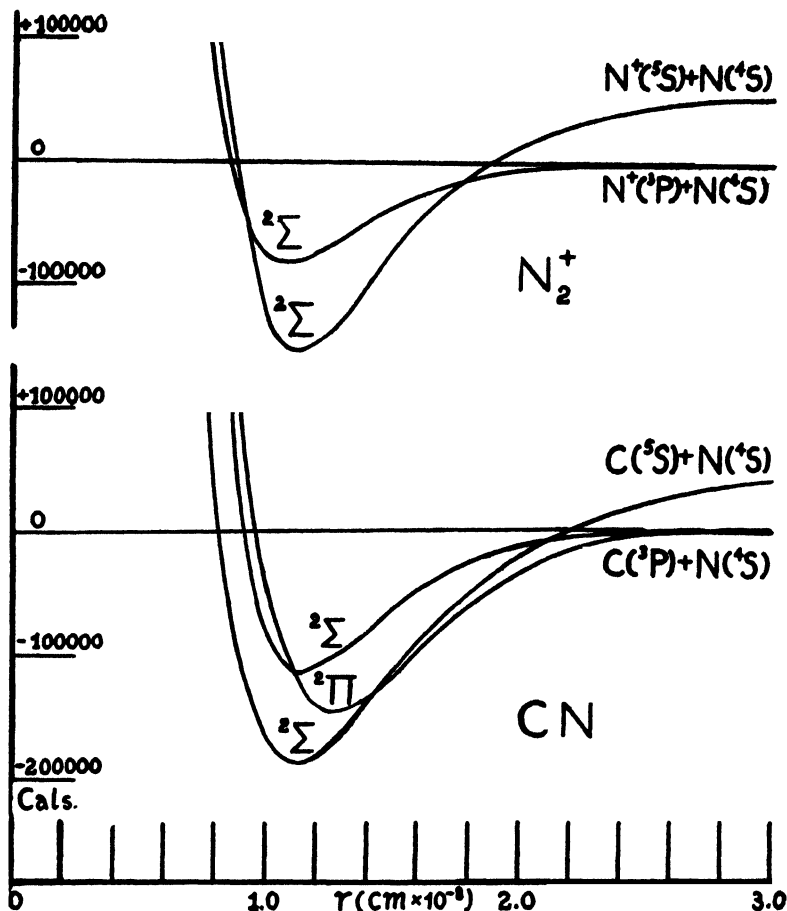


FIG. 6. CURVES REPRESENTING THE POTENTIAL ENERGY $U(r)$ OF THE TWO ATOMS AS A FUNCTION OF THE DISTANCE r BETWEEN THEM

The minimum in each curve is the equilibrium value (r_e) of r ; r_e is the distance between the nuclei for a molecule which is neither vibrating nor rotating. In a vibrating molecule, the vibrations take place between two values of r which correspond to two points of equal energy on the $U(r)$ curve. The exact forms of the $U(r)$ curves are not known except near $r = r_e$ and for $r \gg r_e$; the curves have been merely sketched in a plausible way for other values of r , but must not be considered as accurate. The curves shown represent only the known states of the molecule. Many other curves must exist, some of which must coincide asymptotically for large r , with those shown in figure 6, but most of these doubtless represent unstable molecular states (shallow $U(r)$ curves with large r_e), or highly excited states.

Through an error, the position of the arrow heads in the case of the ϵ bands has been reversed. They should be at the *top* instead of at the *bottom* of the vertical lines indicating the ϵ band transitions.

The two other known states of CN are both formed from a normal nitrogen atom ($V = 3$) and a normal (3P) carbon atom ($V = 2$). Here only two valence bonds are formed, and the heats of formation (145,000 and 113,000 calories for the two states) are much less than for the normal state of CN. Comparing the two cases ($^3P + ^4S$ with $B = 2$ and $^5S + ^4S$ with $B = 3$), we see that the energy lost by exciting the carbon atom from its bivalent 3P to its quadrivalent 5S state is more than compensated by the additional energy gained in the formation of CN. Various other similar cases are known (45). In N_2^+ (44), for example, two $^2\Sigma$ states are known which are exactly analogous to those of CN, the lower (normal) state being derived from 5S excited N^+ plus normal N, the upper from normal (3P) N^+ plus normal N. The relations which are found in CN and N_2^+ are shown graphically in figure 6.

*Relations between atomic and molecular electron configurations;
bonding electrons*

A comparison of the electron configurations of various electron states of molecules with those of their atomic dissociation products suggests some interesting conclusions. Thus in the formation of normal N_2 from $N + N$ (see equation (23)), the correlation between atomic and molecular electrons is probably as follows (45):

$1s^2 + 1s^2$ (closed shells) of $N + N \rightarrow 1s\sigma^2 2p\sigma^2$ of N_2 (closed shells; the $2p\sigma$ electrons are promoted electrons)

$2s^2 + 2s^2$ (closed shells) of $N + N \rightarrow 2s\sigma^2 3s\sigma^2$ of N_2 (closed shells; the $3s\sigma$ electrons are promoted electrons)

$2p^3 + 2p^3$ (valence electrons) of $N + N \rightarrow 3p\sigma^2 2p\pi^4$ of N_2 (closed shells; the $3p\sigma$ electrons are promoted electrons)

The $3p\sigma$ and $2p\pi$ electrons in N_2 may according to this correlation be regarded as the bonding electrons (45), since they are electrons whose spins become paired off when the atoms unite.

In the formation of normal CO from $C + O$, the same relations as for N_2 hold in respect to the $1s^2$ and $2s^2$ atomic electrons ($1s\sigma^2$, $2p\sigma^2$, $2s\sigma^2$, $3s\sigma^2$ in CO). Of the atomic $2p$ electrons the

C atom has two which are valence electrons, while the O atom has four, of which two are valence electrons, while the other two already have their spins paired. These paired $2p$ electrons of the O atom perhaps give the $3p\sigma^2$ closed shell in CO, while the four valence electrons of C + O give the closed shell $2p\pi^4$ of CO (double bond).

In the various states of C + N (see table 2) we have again largely the same correlations, beginning with $1s^2 + 1s^2 \rightarrow 1s\sigma^2 2p\sigma^2$. In $C(^1S) + N(^4S) \rightarrow CN(^2\Sigma)$, we have the $2s$ valence electron of $C(^1S)$ appearing as a still unsatisfied $3s\sigma$ electron in CN, while the $2s^2$ closed shell of $N(^4S)$ appears as $2s\sigma^2$ in CN. The three $2p$ valence electrons in each atom give, as in the case of normal N_2 from $N + N$, the closed shells $3p\sigma^2 2p\pi^4$ (bonding electrons, triple bond). For the two excited states of CN formed from normal C + N ($^3P + ^4S$), we have in the one case ($^2\Pi$) $2p^2(C) + 2p^3(N) \rightarrow 3p\sigma^2 2p\pi^3$ and in the other ($^2\Sigma$) $2p^2 + 2p^3 \rightarrow 3p\sigma 2p\pi^4$. In the former case, two $3p\sigma$ and two $2p\pi$ electrons are the bonding electrons, the third $2p\pi$ electron being an unsatisfied valence electron corresponding to the third $2p$ electron of N. In the latter case, four $2p\pi$ electrons are the bonding electrons, while the one $3p\sigma$ electron is now derived from the third $2p$ electron of N.

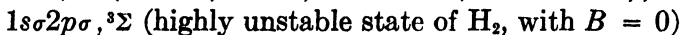
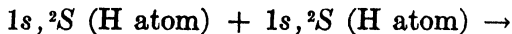
Possible molecular states, and stable molecular states

When two atoms in specified states unite, there are in general several different molecular states which may result. The number and nature of these can be predicted⁹ (42). Of these theoretically possible molecular states, however, in general only one or a few are stable enough to be observed chemically or even spectroscopically. Of the remaining unstable states, some could probably be observed under favorable conditions, while others may have only a momentary existence.

⁹ The possible molecular states resulting from the union of any two atoms in specified states can be definitely predicted (42) at present only in regard to the values of Λ and S , but not in regard to the detailed electron configuration. The problem of the determination of electron configurations has been considered by Hund and the writer (42) and by Herzberg (45), but is not yet finally solved.

Some examples will be helpful. In the union of a carbon atom and a nitrogen atom, each in its normal state (3P and 4S respectively) the theoretically possible states are a $^2\Sigma$, a $^2\Pi$, a $^4\Sigma$, a $^4\Pi$, a $^6\Sigma$, and a $^6\Pi$ state.⁹ Of these the first two are known from band spectra (see table 2 and figure 6); in these two we have $B = 2$, while in the quartet states ($^4\Sigma$ and $^4\Pi$) $B = 1$ and in the sextet states ($^6\Sigma$ and $^6\Pi$), $B = 0$ (see equation (27)). Thus the observed states, which are doubtless the most stable states, are just those in which the number of valence bonds is greatest, in agreement with the London and Heitler theory. In the case of $C(^4S) + N(^4S)$ —see table 2—the possible states are $^2\Sigma$, $^4\Sigma$, $^6\Sigma$, $^2\Sigma$.⁹ Of these, the first, with $B = 3$, is the normal state of the CN molecule; none of the others is as yet known, although it seems likely that the $^4\Sigma$ state, having $B = 2$, is fairly stable and may later be found.

A very simple example is that of two hydrogen atoms each in its normal state. This was the first case considered by Heitler and London. Here we have the following two possibilities:



As Heitler and London showed in their first paper (43) (14), two normal H atoms approaching each other in the manner required to give normal H_2 exert on each other a strong attraction until the two nuclei have approached to a small distance r_* (0.76×10^{-8} cm. for normal H_2) which corresponds to equilibrium.¹⁰ But if the two H atoms approach each other in the manner required to give the unstable $^3\Sigma$ state, they repel each other strongly at all distances, except for a slight van der Waals attraction at large distances. This van der Waals attraction should lead to an equilibrium at some large distance r_* , but the energy of formation for this state of H_2 is doubtless so small that this $^3\Sigma$ state is of negligible stability.

¹⁰ A normal H_2 molecule cannot, however, be directly formed as a result of a collision of two atoms, since it cannot radiate any part of its excess energy (energy of formation). For the actual formation of H_2 , some kind of a collision involving a third body is necessary. This limitation does not, however, apply to all molecules.

In more complex molecules analogous relations hold, except that in general there are a number of molecular states—some stable, some very unstable, others of intermediate stability, as in the example of $C + N$ already discussed (42) (45). In the special case of two atoms, one of which is in a singlet state (as 1S , or 1P , or 1D), we have necessarily $B = 0$, corresponding to an unstable molecular state according to London and Heitler. Thus two normal helium atoms (both $1s^2, ^1S$) should give theoretically one molecular state (14) with $B = 0$ ($1s\sigma^2 2p\sigma^2, ^1\Sigma$), which, however, is without doubt very unstable, so that such molecules are not present in any appreciable numbers in helium gas. In many cases where $B = 0$, however, especially when only one atom is in a singlet state, we know experimentally that molecules of considerable stability can be formed. This may be attributed to the van der Waals forces, which apparently can be of decided importance in cases where the quantum valence forces of Heitler and London are lacking. (In polar molecules, of course, ionic attraction is of primary importance.) Thus normal $Zn(^1S)$ unites with normal $H(^2S)$ to give a normal ZnH molecule ($^2\Sigma$) with a heat of formation, according to band spectrum data, of 21,000 calories. Similar relations, in some cases with even larger heats of formation, exist for the diatomic hydrides of Be, Mg, Ca, Cd, Hg, etc. (46).

The simple theory of non-polar valence as developed by London and Heitler, according to which the stability of a molecule depends on the number of spin pairs formed, is the quantum equivalent of the Lewis theory of valence, but like the latter, is only a first approximation to a complete theory of the energy or stability relations which govern the formation of molecules.

Very much more might be said here about the applications of band spectra to chemical problems, but the object of this paper has been to give an illustrative and suggestive rather than an exhaustive treatment.

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DISCUSSION

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In opening the discussion on Professor Mulliken's paper, I wish to sketch very briefly the change which the study of band spectra is bringing to certain branches of the field of chemistry.

The unit of quantity which has been used by chemistry in the past is the gram molecule or the gram atom; the entire range of quantities used in chemical operations from the most precise quantitative determinations to the largest scale manufacturing processes is not more than a few orders either way from this fundamental unit. As you know, this unit contains some 6.06×10^{23} molecules or atoms and thus, in all classical chemical studies, the number of individual atoms and molecules is very great and only *average* properties are observed.

The characteristic theory of this chemistry has been *thermodynamics*, which is especially suited to the study of systems whose detailed structure is unknown. It gives us the equilibrium conditions of these systems. It is unable to say anything about the velocity with which this equilibrium condition is reached.

The study of atoms and molecules using spectroscopic methods has changed the fundamental unit from the gram atom or molecule to the individual atom or molecule, even though in nearly all spectroscopic experiments we are working with very large numbers of these elementary systems. The spectral line observed visually or on a photographic plate is the result of large numbers of quanta, and so in a sense is the statistical result of these many elementary processes. The line gives us information, however, in regard to one single elementary atomic or molecular process and permits us to build up a more detailed knowledge of the atom or molecule, and this enables us to deduce the macroscopic properties of matter in bulk.

This more detailed knowledge of atoms and molecules permits us to use *statistical mechanics* for our theoretical guidance. Statistical mechanics demands a more detailed knowledge of the elementary units of the macroscopic system, and in turn promises to give us a more powerful attack on problems to which thermodynamics is unsuited. An example of a classical chemical problem solved by this new method is the equilibrium between atomic and molecular iodine (1). The equilibrium for this reaction has been calculated from data of the atomic and molecular spectra alone. It is doubtful if much more complicated examples can be handled in this way, but it is gratifying to know that the fundamental underlying principles and behavior of such a simple equilibrium are understood so well.

In the field of kinetics, where thermodynamics cannot guide us, this spectroscopic information promises to give us a more thorough understanding of the fundamentals. Thus in continuous spectra we see the processes of photochemical dissociation, and in "predissociation," discovered by Victor Henri, we observe a process which enables us to observe indirectly molecules in the process of dissociation.

In these brief remarks, I only wish to emphasize the applications of data of the type presented by Professor Mulliken to ordinary chemical processes. The data are interesting in themselves and illuminate other fields of science which are not so close to classical chemistry.

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ELECTRIC MOMENT, MOLECULAR ORIENTATION AND STRUCTURE IN ALIPHATIC COMPOUNDS

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MATHEMATICAL THEORY OF DIELECTRICS AND EXPERIMENTAL CONFIRMATION

The dielectric constant is generally familiar as a constant in the expression for Coulomb's law and as a quantity to which the capacity of a condenser is proportional, and it is as the latter that it is commonly determined experimentally. It may, however, be conveniently defined from a slightly different point of view. If a difference of potential is set up between two like conducting plates and no medium exists between them, the strength of the electric field at some point between them may be represented by E_0 . If now some medium be allowed to fill the space between the plates, the new field strength E_1 at this point will be proportional to E_0 and equal to E_0/ϵ where ϵ is the dielectric constant of the medium, that is, $\epsilon = \frac{E_0}{E_1}$. It was supposed by Mossotti (34)

and by Clausius (4) that the molecules of the medium acted as perfectly conducting spheres on which charges were induced by the charges on the plates (see figure 1(a)). A negative charge would be induced on the side of the molecule toward the positive plate and an equal positive charge on the side toward the negative plate. The field present before the introduction of the medium is thus opposed and reduced and each molecule becomes temporarily an electric doublet or dipole, the moment of which is the product of one of the induced equal charges by the distance between the two. The simple mathematical development of this assumption, when the medium is a pure substance, leads to the equation:

$$\frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d} = \frac{4 \pi N}{3} \gamma,$$

in which M = the molecular weight, d = the density, N = the number of molecules in a gram-molecule = 6.061×10^{23} , and γ = the molecular polarizability, that is, the moment induced on a molecule by a field of unit strength. γ is a constant characteristic of the substance. This expression, called the molar polarization, is, in many cases, found approximately equal to the Lorentz (24)-Lorentz (23) expression for molar refraction, $\frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d}$, as would

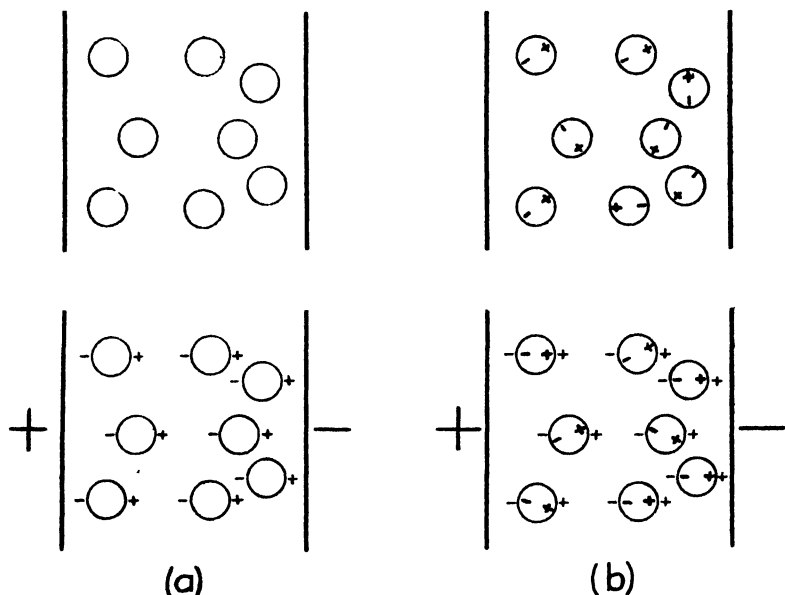


FIG. 1. MOLECULAR THEORY OF DIELECTRICS ACCORDING TO (a) MOSSOTTI AND CLAUSIUS AND (b) DEBYE

be expected from the well-known Maxwellian (31) relation $\epsilon = n^2$. For many substances, however, when n , the index of refraction measured for light in the visible region, is extrapolated to the region of long electric waves in which the dielectric constant is measured, ϵ is found to be much larger than n^2 . For these same substances, the molar polarization, which will be represented by P , is found to depart from the constancy required by the Clausius-Mossotti equation and vary considerably with temperature.

Debye (6) (7) has applied to dielectrics a treatment analogous to that used by Langevin (20) in discussing paramagnetism, assuming that a molecule may contain a permanent doublet of moment, μ , which causes the molecule to become oriented in an electric field (see figure 1(b)). If all the molecules were oriented in the applied field so that the axes of their doublets lay in the direction of the field, the permanent moment μ would be added to the induced moment γ in the Clausius-Mossotti expression for the polarization, but orientation of the molecules containing the doublets is opposed by the thermal agitation of the molecules, which, of course, varies with the temperature, so that the polarization becomes a function of the temperature. Debye has expressed this relation as

$$\frac{\epsilon - 1}{\epsilon + 2} \frac{M}{d} = \frac{4\pi N}{3} \gamma + \frac{4\pi N}{3} \frac{\mu^2}{3kT},$$

in which k = the molecular gas constant = 1.372×10^{-16} , and T = the absolute temperature. $\frac{\mu^2}{3kT}$ is the mean component of the moment per molecule in the direction of an internal field of unit strength and it is this, instead of μ , which is added to γ . As T is the only variable on the right-hand side of the equation, it is evident that, when the molecule contains no permanent doublet ($\mu = 0$), the second term on the right drops out and the equation becomes equivalent to the Clausius-Mossotti expression, which takes account only of doublets induced in the molecules. However, when the molecule is unsymmetrical electrically, containing a permanent doublet, the polarization is a linear function of $\frac{1}{T}$ and the second term on the right may be much larger than the first.

The equation may be written in the form:

$$P = a + b/T,$$

in which $a = \frac{4\pi N}{3} \gamma$ and $b = \frac{4\pi N \mu^2}{9k}$. When ϵ and d are measured over a range of temperature, the values of the constants a and b

may be calculated and the value of μ obtained from that of b . a may also be calculated approximately as the molar refraction for infinite wave length obtained by extrapolation of the refraction in the visible region. b/T is then given as the difference between a and P at one temperature. This method of obtaining the moment is somewhat less accurate and is misleading when any molecular association occurs.

In the derivation of this equation on the basis of the classical mechanics, it is necessary to suppose that, in the absence of an external field, the molecules are oriented at random. The first applications of the principle of quantized orientation to the problem led to an equation of the same general form but with a different coefficient for the second term (35) (36). However, applications of the new quantum mechanics to simple poly-atomic molecules have given equations from which results practically identical with those of the Debye equation may be obtained (18) (32) (30) and Van Vleck (63) has recently given a general proof of the equation on the basis of the new mechanics.

Obviously, when the molecules are not entirely free to orient in an applied field, the equation cannot be expected to apply. For gases, the dielectric constants of which are very close to 1, simplification may be effected by setting $\epsilon + 2$ equal to 3. The validity of this simplified equation has been established experimentally by Jona (15), Zahn (75) (76) (77), Sanger (39), Stuart (59) (60), and others (65) (54a). In liquids, the molecules are so close together that large doublets attract one another strongly, forming complex molecules or restricting one another's freedom of motion. When the doublets are sufficiently separated from one another by the molecules of a non-polar solvent, they should behave much as if in the gaseous condition.

The polarization $P_{1,2}$ of a mixture of two substances 1 and 2 is expressed by Debye as:

$$P_{1,2} = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{c_1 M_1 + c_2 M_2}{d} = c_1 P_1 + c_2 P_2,$$

in which c_1 and c_2 = the mole fractions, M_1 and M_2 = the molecular weights, and P_1 and P_2 = the polarizations of substances 1

and 2 respectively. Written in the form: $P_2 = \frac{P_{1,2} - P_1}{c_2} + P_1$

the expression may be used to calculate P_2 when P_1 is known. If substance 1 is non-polar, its value of b is 0 and P_1 is equal to the constant a , which is the molar refraction for light of infinite wave-length. Since measurements of refraction shortly to be published (51) show that the molar refractions of a variety of substances in mixtures are independent of their concentrations,

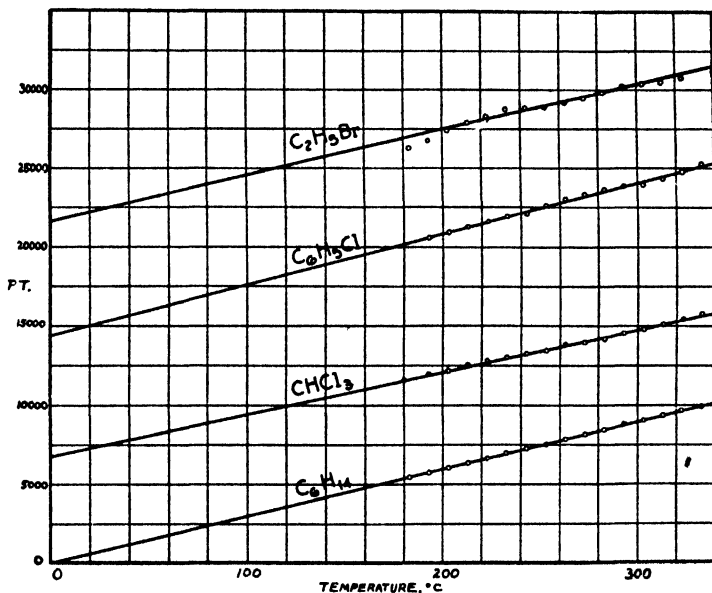


FIG. 2. VARIATION OF PT WITH T

the value of P_1 may be regarded as constant and used to calculate P_2 . If P_2 is obtained for several values of c_2 and the results extrapolated to $c_2 = 0$, that is, to infinite dilution, the mutual effects of the doublets in neighboring molecules should be eliminated and the polarization should be the same as in the gaseous condition at the same temperature. Lange (19) and Williams (67a) and his collaborators have obtained the same results for the extrapolated values of P_2 in different solvents. Figure 2, in which the extrapolated values of P multiplied by T are plotted

against T , shows the excellent conformity of some diluted polar liquids to the Debye relation and a similar linearity has been obtained in the results for several other liquids as yet unpublished. Table 1 shows very satisfactory agreement between the values of the moment in the liquid condition and those in the vapor calculated by means of the Debye equation.

In the majority of the determinations of electric moment in the liquid condition, the dielectric constant and density are measured at one temperature only, so that it is impossible to calculate the induced polarization from these measurements alone.

TABLE 1
Electric moments ($\times 10^{18}$) in the liquid and vapor states

	LIQUID	VAPOR
H ₂ O.	1.8 (67)	1.8 (60)
CH ₃ OH.	1.64 (58)	1.67 (33)
C ₂ H ₅ OH.	1.74 (58)	1.69 (33)
C ₂ H ₅ OH.	1.74 (57)	1.66 (33)
(C ₂ H ₅) ₂ O.	1.22 (67a)	1.14 (60)
(CH ₃) ₂ CO.	2.71 (17) (73)	2.84 (60)
CHCl ₃	1.05 (53)	1.05 (43a)
C ₂ H ₅ Br.	1.86 (53)	1.78 (29)
C ₂ H ₅ I.	1.66 (57)	1.62 (29)

As has been stated, the induced polarization, $\frac{4\pi N}{3} \gamma = a$, com-

monly differs little from the molar refraction, $\frac{n^2 - 1}{n^2 + 2} \frac{M}{d}$. Conse-

quently, when the latter is subtracted from the total polarization P , a value is obtained for b/T , which, in most cases, is not seriously inaccurate and may be used to calculate the moment. However, the molar refraction for light in the visible region arises mainly from the action of the electrons in the rapidly alternating field of the light wave and, when extrapolated to infinite wave-length, which is practically equivalent to the wave-length used in determining the dielectric polarization, does not contain the contribution of the shifts of atoms or groups of atoms which may be induced by the relatively slow alternating electric field used in the

dielectric constant measurement. This contribution, which may be termed the atomic polarization P_A , is usually small and may at times be practically negligible in comparison with the electronic contribution or extrapolated refraction for infinite wave-length, P_E . The sum, $P_E + P_A = a$, may be determined not only from the temperature variation of the total polarization, but also as the polarization in the solid state where the dipole contribution is eliminated by the fixing of the molecules. The atomic polarization has been considered by the writer (49). The conclusion has been reached that it is generally not an additive property, but tends to be greater, the greater the number of atomic nuclei or groups in the molecule, the greater the number of electric doublets, and the more unsymmetrical the arrangement of these doublets in the molecule and that, in the calculation of the electric moment, it may be disregarded without risk of introducing appreciable error only when the moment is large and the molecule small.

Some years ago, when few values were available for the study of the relation between electric moment and molecular structure, the writer (46) (47) used a modified form of an equation developed by Gans (13) to calculate the moments of a large number of molecules. As the equation attempted to take into account, in approximate fashion, the mutual effects of neighboring molecules, which cannot be treated accurately, and as certain of its assumptions are open to criticism (7), the values of the moments obtained with it might be expected to be only very approximate. However, as many of these values are now in use in the literature, it seems desirable to compare them with the values obtained with the Debye equation from more recent measurements upon gases or dilute solutions and obtain an estimate of their accuracy. In the calculation by the modified Gans equation, the quantities used in the Debye equation are required at one temperature only and in addition the molecular diameter is used in an attempt to evaluate the effect of the molecular field. The values thus obtained for typical substances in the liquid condition are shown in table 2 in the column headed "Calculated," while the column headed "Observed" gives values which should be correct to within 0.1×10^{-18} , being better than this in many cases.

The expression for the induced polarization in the Gans equation is identical with that in the Debye equation so that the part played by the atomic polarization is the same in both. Disregard of P_A , the values of which were unknown when these calculations were made, introduced errors into the moments of substances for which small values were found. The moments calculated for benzene and carbon tetrachloride are probably due to this cause and it has been pointed out by the writer in the

TABLE 2

Electric moments ($\times 10^{18}$) calculated by modified Gans equation and observed by other methods

	CALCULATED (46)	OBSERVED
Hexane	0	0 (53)
Benzene	0 2	0 (38)
Toluene	0 4	0 4 (67a)
Methyl alcohol	1.78	1.67 (33)
Butyl alcohol	2 06	1 66 (33)
Ethyl ether.....	1 37	1 14 (60)
Hydrogen sulphide.....	1 02	1.10 (2)
Acetone	2 08	2.84 (60)
Methyl ethyl ketone	2 29	2 79 (73)
Aniline.....	1 35	1 51 (14)
Ethyl acetate	1 62	1.74 (17)
Hydrogen chloride	1.07	1.03 (75)
Hydrogen bromide	0 92	0 79 (75)
Hydrogen iodide	0 64	0 36 (75)
Ethyl bromide	1 56	1 86 (53)
Chlorobenzene	1 42	1.52 (53)
Bromobenzene.....	1.39	1.5 (69)
Chloroform.....	1 25	1 05 (53)
Carbon tetrachloride	0 48	0 (39)

paper (49) just referred to that neglect of P_A may give rise to even larger apparent values for molecules possessing no moment. Actually, some of the experimental data for benzene indicated that the moment was zero and it was recognized that the value calculated was not of sufficient accuracy to be distinguishable from zero.

The good agreement between the calculated value for liquid methyl alcohol and the accurate value obtained for the vapor is

due not to the excellence of the method of calculation but to some compensation between the complicated effects of orientation in the liquid. The reasonable accuracy of the values obtained by some investigators who measured alcohols in solutions without using considerable dilution or variation in temperature may also be attributed to this compensation. The fact that the calculation gave different values for the moment at different temperatures in supposedly associated liquids showed that the Gans equation did not take care of the effect of molecular association. The increase in the calculated values of the moment with increasing length of the carbon chain in the alcohols, ketones, and some other series must now be attributed mainly to change in the effect of molecular association. Among the halides the calculated values show fairly satisfactory agreement with the accurately observed values, and, in general, the less strongly associated substances show not unsatisfactory agreement. It is evident then that this method of calculation commonly gives fairly accurate values of the moments of molecules which are not strongly associated, although conclusions cannot safely be drawn from small differences between these values; but in strongly associated liquids the equation cannot be relied upon to give results of any significance, although it often gives the order of magnitude of the moment.

DISTRIBUTION OF ELECTRICITY AND ELECTRIC MOMENT OF THE MOLECULE

The mutual effects of the doublets in neighboring molecules may be better understood if the relation of the doublets to molecular structure is considered. In view of the uncertainty and the rapidity of change in the hypotheses of atomic structure and our ignorance of the fundamental nature of the chemical bond, it is impossible to assign definite electronic arrangements to the atoms in a molecule. It is generally believed, however, that a single chemical bond involves a pair of electrons and the electrostatic effect of the charge in the molecule is represented by picturing certain locations in the structure as occupied by the electrons. The consideration of these locations makes possible the discussion of the distribution of the electricity in the molecule.

The argon atom is believed to consist of a positive nucleus with 18 electrons distributed about it, the total charge of the atom being zero. The symmetry of the distribution is such that the mean position of the center of gravity of the electrons is coincident with that of the positive nucleus, the atom thus having no permanent moment. When the atom is placed in an electric field the electrons shift so that their center of gravity is no longer coincident with the positive nucleus, the system thus temporarily forming an electric doublet as do the molecules in figure 1(a). Since the molecule contains no permanent doublet, the second term in the Debye equation is zero and the polarization should, therefore, be constant. The chloride ion, Cl^- , is supposed to consist of a symmetrical arrangement of 18 electrons around a nucleus which has 17 positive charges. Since the center of gravity of the electrons coincides with the positive nucleus, the system of charges may, as an approximation, be resolved into a single negative charge located at the nucleus. If, now, a hydrogen nucleus could, without distortion of the system, be attached to form a neutral hydrogen chloride molecule, a permanent electric doublet should result. The moment of the doublet should be the product of the single electronic charge, 4.774×10^{-10} e.s.u., by the distance between the nuclei, which has been calculated from infra-red absorption spectra as 1.27×10^{-8} cm. The moment 6.06×10^{-18} calculated in this way is far larger than the value 1.03×10^{-18} obtained by application of the Debye equation to measurements of the dielectric constant of gaseous hydrogen chloride, because the positive hydrogen nucleus draws the electrons of the chloride ion toward it, distorting the system of charges and greatly diminishing the distance between their centers of gravity. The extent of the distortion has been calculated to be of approximately the right amount to cause the difference between the values of the moments calculated from the molecular structure and those obtained from experimental data (45). When placed between the plates of a condenser, the hydrogen chloride molecules orient in the externally applied field as far as permitted by the thermal agitation and the effect of the induced doublet is superimposed upon that of the permanent.

The treatment of the system of positive and negative charges in the molecule as giving rise to a single doublet is a rough approximation even in the simpler molecules. In more complex molecules, the structure should act as a single doublet only at a considerable distance. The oxide ion, O^{--} , may be regarded as a symmetrical structure, just as was the chloride ion. If two hydrogen nuclei are attached to form a water molecule, two electric doublets should be formed, the positive end of each being a hydrogen nucleus. If the two portions were on opposite sides of the molecule and equidistant from the oxygen nucleus which lay on the straight line joining them, the two doublets would cancel one another and the moment of the molecule as a whole would be zero. The considerable moment, 1.8×10^{-18} , found for the molecule may be very satisfactorily explained by supposing that the two doublets make an angle with one another and, consequently, give a considerable resultant moment. It was calculated by the writer (46) that, if the structure of the methyl group could be regarded as that of a regular tetrahedron, it should be possible to substitute it for that of a hydrogen atom without directly altering the moment of the molecule, provided that the hydrogen nuclei in the methyl group were at the same distance from their binding electron pairs as was the replaced hydrogen nucleus from its bonding pair, and provided further that there were no alteration in the hypothetical position of the electron pair to which the original hydrogen, now replaced by methyl, was attached. This is contrary to the idea of a varying electronegativity among hydrogen and the alkyl radicals, which will be discussed later, and cannot be expected to be true in all cases. Thus, in hydrogen chloride, bromide, and iodide, the proton is thought to penetrate the halogen structure somewhat (1), thereby shortening the distance between the positive and negative centers of gravity. Such penetration cannot occur when the hydrogen is replaced by methyl, so that the distance between the electrical centers of gravity is greater and the moments observed for methyl chloride, bromide, and iodide are considerably higher than those of the corresponding hydrogen halides. However, when one of the hydrogens in the water

molecule is replaced by a methyl group to form methyl alcohol, little change in moment occurs and a hydrogen of the methyl may be replaced by another methyl to form ethyl alcohol and, indeed, the hydrocarbon chain may be lengthened to give octyl alcohol without causing an appreciable change in moment (see table 3). On the other hand, if the hydroxyl hydrogen in methyl alcohol is replaced by methyl, there is a repulsion between the two methyl groups because of their bulk which widens the angle between the two doublets, thereby decreasing the resultant moment of the molecule. Further increase in the size of these groups to ethyl increases the repulsion between them and further widens the angle between the doublets, so that the moment observed for ethyl ether is slightly lower than that for methyl, although the difference is much less than that between methyl ether and methyl

TABLE 3
Electric moments ($\times 10^{18}$) of water, alcohols, and ethers

HOH.....	1.8 (60, 67)		
CH ₃ OH...	1.67 (33)	CH ₃ OCH ₃	1.29 (60)
C ₂ H ₅ OH	1.69 (33)	C ₂ H ₅ OC ₂ H ₅	1.14 (60)
<i>n</i> -C ₃ H ₇ OH	1.75 (58)	CH ₂ \	
<i>n</i> -C ₄ H ₉ OH.	1.66 (33)	O	1.88 (60)
<i>n</i> -C ₈ H ₁₇ OH.	1.70 (57)	CH ₂ /	

alcohol. In ethylene oxide, the same doublets should exist as in methyl ether and methyl alcohol; but the positive ends of the doublets are drawn together because of the bond between the carbons and the angle between the doublet axes is thus made less than in the alcohol, so that the resultant moment is larger as shown in table 3.

EFFECT OF THE SIZE AND LOCATION OF THE ELECTRIC DOUBLETS IN THE MOLECULE UPON MOLECULAR ORIENTATION

In the water molecule, the positive ends of two large doublets lie near the surface causing a very strong field of force around the molecule, so that the molecules affect one another greatly, strong association occurs, and the liquid is highly abnormal. In methyl alcohol the doublets may be supposed to have the same

location with reference to the oxygen that they have in the water molecule, but one of them is screened by the methyl group which cuts down its field outside of the molecule, thereby reducing the effect of the molecule upon its neighbors and rendering methyl alcohol less abnormal than water. The screening effect is slightly increased when methyl is changed to ethyl and, as the hydrocarbon chain lengthens in going up the series of the alcohols, the doublets in adjacent molecules approach one another less frequently and the abnormality of the liquids diminishes. However, the strong field of force around the OH doublet still remains and *n*-octyl alcohol shows a great variation of P_2 with the concentration of its solution in benzene and in heptane (57). When the hydroxyl hydrogen of ethyl alcohol is replaced by an ethyl group to form ether, the unscreened doublet is shielded and the field of force around the molecule is so reduced that the liquid is quite normal and, in solution in benzene, the polarization of ether is independent of concentration (7), although the moment is still $\frac{2}{3}$ that of the alcohol.

Ethyl bromide (table 2), in spite of the moment, 1.86×10^{-18} , possessed by its molecule, is ordinarily termed a normal liquid. Its doublet should lie in the region of attachment of the ethyl group to the bromine atom and should thus be screened not only by the ethyl group but also by the large bromine atom, which should greatly reduce the molecular field as compared to that of the ethyl alcohol molecule. In ethyl iodide, the screening effect of the large iodine atom should be greater than that of the bromine atom, and this, taken in conjunction with the slightly smaller moment of the molecule, 1.66×10^{-18} , should give a smaller molecular field. Measurements of the partial vapor pressures of binary mixtures (50) show the abnormalities resulting from the very strong forces exerted by the alcohol molecules, while the effect of the forces is much less in the case of ethyl bromide and, for ethyl iodide, slightly less than for ethyl bromide.

It is difficult to construct a completely satisfactory picture of the interaction of the molecular force fields. The effect of the molecules upon one another must depend not only on the size of their doublets, but also upon the location of the doublet or dou-

plets in the molecule, and upon the mere geometrical shape of the molecule. It is not difficult to picture the molecules of a liquid possessing no electric moment as roughly oriented merely because of their shapes, such an orientation as that found by Stewart (55) for the isomeric heptanes. There are two possible simple orientations which two doublets in adjacent molecules might be expected to adopt relative to one another (figure 3). The negative end of one doublet might attract the positive end of the other so that the axes of the two doublets would fall in line and the two would support one another (figure 3, I). The attraction between the ends would lengthen each separate doublet giving a moment for the two together greater than 2μ , μ being the moment of each doublet alone. If the force of attraction were so great that the

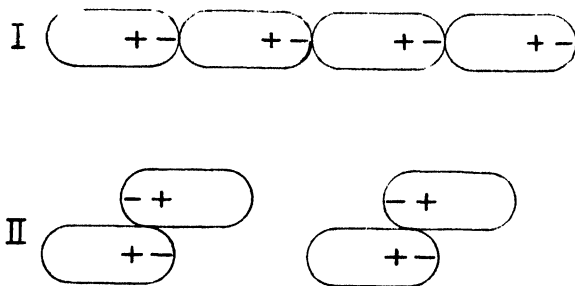


FIG. 3. TYPES OF ORIENTATION OF DIPOLE MOLECULES

two molecules actually associated to form a double molecule, the number of molecules in the liquid would be cut in half, but, since in the Debye equation the moment of the molecule is squared, we should have in the expression for the polarization a quantity somewhat greater than $4\mu^2$ instead of μ^2 and the polarization would, therefore, be increased in spite of the reduction in the number of molecules. Even if the two molecules were not definitely associated to act as one, they would attract one another and tend to orient more or less with respect to one another so that when a field was applied externally to measure the dielectric constant, the orientation would be greater than that calculated. The shape of the molecules would commonly prevent an exact lining up of the doublets and their axes would, consequently,

make an angle of somewhat less than 180° with one another. As this angle decreases, the polarization diminishes and the common effect of orientation is to decrease the polarization instead of increasing it. When the angle between the axes becomes zero, that is, when the doublets are parallel and pointing in opposite directions, (figure 3, II), the moments cancel one another and the doublet contribution, the second term of the Debye equation, becomes zero. This position of the doublets, which represents the other extreme of the two possible simple orientations, would result in a polarization for a polar substance differing little from its molar refraction. More than two molecules would tend to line up if the first type of orientation prevailed and one might imagine a polarization built up almost indefinitely in this way. Also, more than two molecules may possibly orient in some complex arrangements which either increase or decrease the polarization. The stability of the orientation of one molecule relative to another must depend to some extent upon the forces exerted upon it by the other neighboring molecules. It appears probable, therefore, that, when there is not much difference between the energies of two different orientations, one orientation may change to the other as the mean distance between the dipole molecules changes. Thus, when a polar liquid is dissolved in a non-polar, the orientation of the polar molecules relative to one another may change from one type to another with change in concentration. Of course, when the polar molecules are in very dilute solution and, on the average, far away from one another, they should assume a random orientation unless they actually associate to form a definite complex molecule which is not much dissociated even in the dilute solution, as appears to be the case with acetic acid in benzene solution (37) (53a). Change in temperature also might affect the type of orientation. It must be borne in mind that the supposed orientation which has been discussed is not complete and, indeed, may be little more than a condition in which a tendency toward a certain arrangement of the molecules exists. As orientation is opposed by thermal agitation, rising temperature reduces the abnormalities of liquids and conformation to the Debye equation becomes closer.

Dolezalek (8) (9) and many others (41) have explained the deviation of a physical property of a mixture from linear dependence upon the composition of the mixture by assuming a definite chemical equilibrium between single and complex molecules, the value of the property observed depending upon the proportions of the different complex and single molecules in the mixture. Although this is probably true in some cases, the method has been carried to such extremes as not infrequently to involve most improbable assumptions and, in most cases, merely to give equations which, because they contain a sufficient number of adjustable constants, provide adequate means of representing the experimental results. The variation of the polarization of a polar substance with its concentration in solution in a non-polar substance may be represented quantitatively by assuming that a portion of the single molecules associates to form definite double molecules which possess a different moment from those of the single, the moment usually being assumed to be zero. The assumptions involved are necessarily arbitrary, and the only indication that they correspond to the facts is given by the manner in which the equations with their adjustable constants are able to represent the experimental data. Acetic acid in dilute solution in benzene is shown by molecular weight determinations to consist largely of double molecules which are shown by dielectric constant measurements, as yet unpublished, to possess little or no moment. In a solvent in which these double molecules are largely dissociated in dilute solution, it may be possible to represent correctly the change of polarization with concentration in terms of the equilibrium between the single and the double molecules.

Debye (7) has developed an equation which represents neighboring doublets as orienting one another in such a way as to increase the polarization, and has found that it fits satisfactorily the variation of the polarization of ethyl alcohol with its concentration in dilute solution in benzene. This equation can, however, represent orientation as effecting only an increase and never a decrease in polarization. The writer, in unpublished work, has developed an equation from the approximate equation

of Gans (13), which satisfactorily reproduces the variation of the polarization of ethyl bromide in hexane not only with concentration but also with temperature. This equation can, however, represent orientation as bringing about only a decrease and never an increase in polarization. In view of the number of factors which determine the effects of the doublets upon one another, factors which cannot be quantitatively evaluated, it appears impossible to formulate any generally valid expression for the interaction of the molecular doublets, which will be much more than an empirical equation. It is possible, however, to show

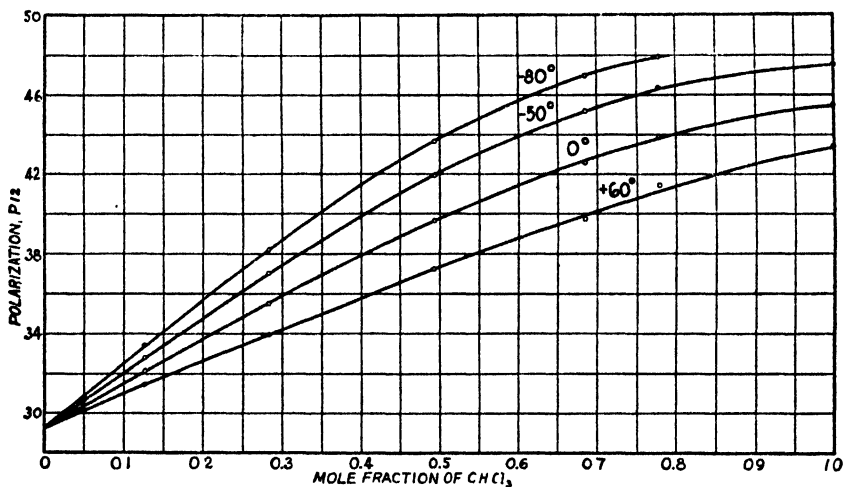


FIG. 4. MOLAR POLARIZATIONS OF HEXANE-CHLOROFORM MIXTURES

qualitatively how the different factors which have been discussed affect the polarizations of typical polar substances.

The $P_{1,2}$ -composition curves may be advantageously considered. If there were no intermolecular action, each curve would be a straight line, the tangent to the observed curve at $c_2 = 0$. This is nearly the case for the hexane-chloroform mixtures (53) (figure 4) at 60° , where the $P_{1,2} - c_2$ curve shows almost no deviation from linearity, but, as the thermal agitation decreases with decreasing temperature, the mutual effects of the doublets in the chloroform molecules, the moments of which are only $1.05 \times$

10^{-18} , increase and the curvature becomes more pronounced. The curvature is greater in the somewhat similar curves for the hexane-chlorobenzene mixtures (53) for the larger moment of the chlorobenzene molecules, 1.52×10^{-18} , makes them affect one another more strongly. In the hexane-ethyl bromide mixtures (53) (figure 5), the strong forces exerted by the large doublets ($\mu = 1.86 \times 10^{-18}$) in the ethyl bromide molecules actually cause the curves to pass through a maximum which becomes

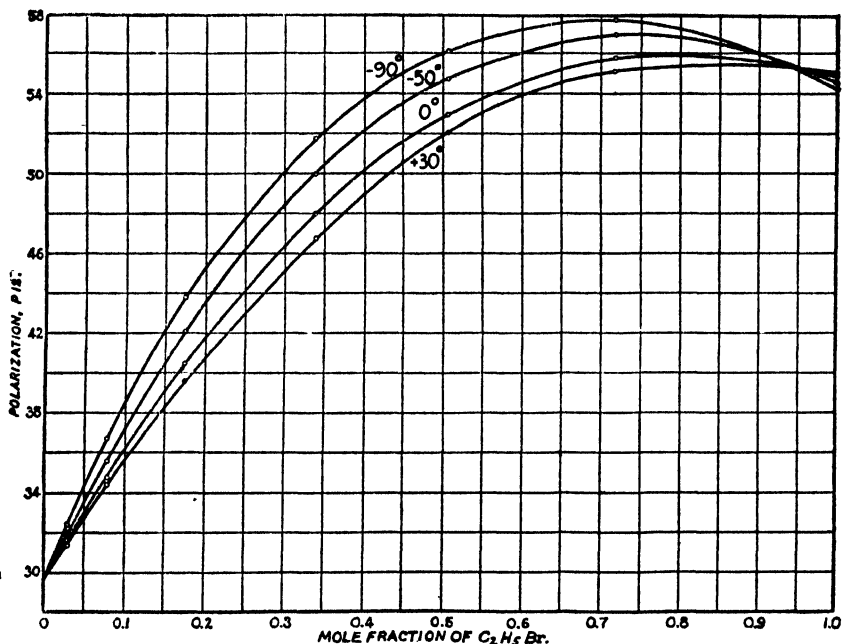


FIG. 5. MOLAR POLARIZATIONS OF HEXANE-ETHYL BROMIDE MIXTURES

flatter and flatter as the increased thermal agitation accompanying increasing temperature diminishes the orienting effects of the molecules upon one another. The intersection of the curves for different temperatures indicates a mixture containing 0.95 mole fraction of ethyl bromide as having a polarization independent of temperature. The polarization of pure ethyl bromide increases slightly with increasing temperature instead of decreasing as required by the Debye equation, but the dielectric constant

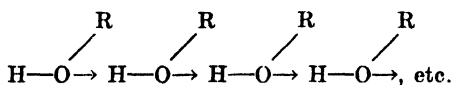
decreases. The behavior of ethyl iodide in heptane (57) is very similar to that of ethyl bromide in hexane. The slightly smaller moment, 1.66×10^{-18} , and the slightly greater screening of the doublet by the larger iodine atom reduces the molecular field somewhat, so that the curvature of the $P_{1,2} - c_2$ curves is a little less pronounced and the polarization of pure ethyl iodide decreases very slowly with rising temperature instead of increasing like that of ethyl bromide. As the hydrocarbon chain attached to the halogen lengthens, the number of doublets per unit volume diminishes and their effect upon one another therefore decreases, butyl bromide showing less deviation from linearity in the $P_{1,2} - c_2$ curves (37) and heptyl bromide much less.

The interaction of the dipoles in all these molecules decreases the polarization in the manner of the second type of orientation discussed, in which the doublets orient in such a way as to oppose and at least partly cancel one another. This is the effect observed in the great majority of the substances thus far studied, as might be expected from considerations of molecular structure. A doublet or small group of doublets which resolve themselves into one, usually lies at one end or side of the molecule with the bulk of the molecule behind it. An orientation of the first type necessitates a lining up of the molecules with the axes of the doublets more or less in line and the bulk of a molecule between each doublet and its neighbor in line as in figure 3, I. The screening effect of the bulk of the molecule should so reduce the forces between the doublets as to render the orientation unstable. The more probable orientation is the second type, in which the axes of the doublets tend to become more or less parallel to one another pointing in opposite directions as in figure 3, II.

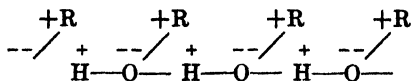
The behavior of the alcohols in solution in benzene (7) (57) may be explained by supposing that both types of orientation occur. In the very dilute solutions, the amount of orientation is slight and extrapolation of P_2 to infinite dilution gives values which conform approximately to the Debye equation. As the concentration of the alcohol increases, orientation increases and, apparently, orientation of the first type predominates since the polarization increases. However, as the concentration increases, the

second type of orientation appears to become more stable than the first and gradually to predominate, causing the polarization of the alcohol to reach a maximum and then decrease. Debye (7) has suggested a triangular arrangement of three molecules to account for the decrease in polarization in the concentrated solutions. It is not impossible that a more complex arrangement of the molecules may exist, but the supposition of the simple orientation of the second type is in accord with the conclusions of Stewart and Skinner (56) from x-ray studies, that in the pure normal alcohols the molecules are usually paired with the hydroxyl group in contact with one another.

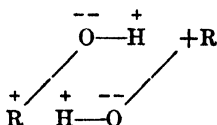
The theory of a proton sharing a pair of electrons with each of two groups proposed by Latimer and Rodebush (22) has been applied by Sidgwick (43) to the association of the alcohols. Sidgwick states that "the great majority of associated substances contain a hydroxyl group," polymerization arising through the hydroxyl "hydrogen acting as acceptor and the oxygen as donor," that is, the hydrogen of one hydroxyl group becomes attached to the oxygen of the hydroxyl of another molecule and, as a result, shares electrons with both oxygens. Alcohol molecules would associate thus:



This actual sharing of electrons between molecules to form a complex has been criticised by the writer and his collaborators (51) on the ground that it would cause a small decrease in the molar refraction of the alcohol which is not observed experimentally. However, this arrangement of the molecules relative to one another would correspond to an orientation of the first type and would thus cause an increase of polarization as observed in the dilute solutions of the alcohols in benzene. A rough idea of this may be given by writing the + and - signs of the doublets in the formula:



There appears to be no reason why the mere attractive force of the doublets for one another should not bring about an orientation of the molecules roughly approximating this without any actual sharing of electrons between them. This would account only for the increase in polarization observed in the more dilute solutions. The decrease observed in the more concentrated solutions could be explained by an orientation like the following:



One might assume, according to Sidgwick's method, that each hydrogen shares a pair of electrons with each of the two oxygens or that only one hydrogen does so, but, in either case, the assumption appears artificial. The mere attraction of the doublets for one another should be able to cause the orientation to occur to an extent sufficient to account for the observed behavior. This of course, cannot be regarded as evidence against Sidgwick's theory, but, added to the evidence against it given by the constancy of the molar refractions of the alcohols in solution, we now have the fact that the complex molecule proposed by him is able to account for the behavior of the polarization in dilute solution only. It is necessary to assume the formation of a second type of complex molecule to account for the behavior in concentrated solution.

It appears much simpler to suppose that, in the dilute solutions at higher temperatures, the molecules tend to arrange themselves in an orientation of the first type. The increased effect of the moments gives an increased potential energy to this orientation as the internal field of the liquid increases with increasing concentration of the alcohol. The increased potential energy decreases the stability of the orientation, which tends, therefore, to change over into one of the second type in which the doublets more or less cancel one another so that the potential energy of the system diminishes. This hypothesis does not explain entirely the behavior of the alcohols in solution in hexane and heptane, in which

TABLE 4
Dielectric constants, polarizations, and refractions of isomeric octyl alcohols at 25°C.

	ϵ	P	MR _D		ϵ	P	MR _D
C-C-C-C-C-C-C-OH	9.8	118.3	40.68	C-C-C-C-C-C-C-OH	3.58	75.5	41.43
C-C-C-C-C-C-C-OH	7.7	110.1	40.64	C-C-C-C-C-C-C-OH	7.16	106.9	40.28
C-C-C-C-C-C-C-OH	6.8	104.9	40.41	C-C-C-C-C-C-C-OH	3.46	72.8	40.93
C-C-C-C-C-C-C-OH	5.0	91.0	40.61	C-C-C-C-C-C-C-OH	5.4	100.1	41.65
C-C-C-C-C-C-C-OH	9.8	118.6	40.72	C-C-C-C-C-C-C-OH	6.00	99.6	39.99
C-C-C-C-C-C-C-OH	7.1	106.9	41.01	C-C-C-C-C-C-C-OH	5.15	95.1	41.28
C-C-C-C-C-C-C-OH	4.37	85.4	41.30	C-C-C-C-C-C-C-OH	3.76	75.4	40.35
C-C-C-C-C-C-C-OH	2.85	63.1	42.21	C-C-C-C-C-C-C-OH	3.44	71.0	40.51

$\begin{array}{c} \text{C} \\ \\ \text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{OH} \end{array}$	4.95	92.6	41.41	$\begin{array}{c} \text{OH} \\ \\ \text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C} \\ \\ \text{C} \end{array}$	2.92	61.8	40.50
$\begin{array}{c} \text{C} \quad \text{OH} \\ \quad \\ \text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C} \\ \\ \text{C} \end{array}$	5.9	100.5	41.08	$\begin{array}{c} \text{OH} \quad \text{C} \\ \quad \\ \text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C} \end{array}$	7.18	104.8	39.61
$\begin{array}{c} \text{C} \quad \text{OH} \\ \quad \\ \text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C} \end{array}$			40.82	$\begin{array}{c} \text{OH} \quad \text{C} \\ \quad \\ \text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C} \end{array}$	3.36	70.6	40.64

the forces between the doublets are presumably a little greater than in benzene because of the somewhat smaller dielectric constant of the solvent. More extensive investigations must be carried out on these solutions before their behavior can be safely explained.

As the electric moments of all the alcohols thus far measured, including *n*-octyl (see table 3), differ little from 1.7×10^{-18} , it is reasonable to suppose that the various isomeric octyl alcohols have moments not far from this value. The dielectric constants of the nine isomeric heptanes differ from 1.93 by no more than 0.015 and their polarizations differ from 34.5 by no more than 0.26 (54). If no molecular orientation or association occurred, the polarizations and dielectric constants of the octyl alcohols should be approximately the same, being calculable by means of the Debye equation from the little differing molar refractions and densities and the moment 1.7×10^{-18} . The values thus obtained are 5.9 for the dielectric constant and 100 for the polarization at 25°. In table 4 are listed the dielectric constants, molar polarizations, and molar refractions of twenty-two isomeric octyl alcohols prepared by Mr. H. B. Glass and Mr. G. B. Malone working with Professor E. Emmet Reid. The dielectric constants were measured by Mr. W. N. Stoops and the polarizations and refractions were calculated from these values and from the densities and refractive indices determined by Messrs. Glass and Malone. The quantities of the materials available were, with two exceptions, insufficient to permit of study in solution and consequent determination of the electric moments. In the formulae given for the alcohols the hydrogens are omitted in order that the positions of the hydroxyl group and the branching of the carbon chain may be more readily apparent.

It is evident that the type of orientation predominating in the alcohol depends upon the location of the hydroxyl group in the molecule. When the doublets are at the end of a long carbon chain and remote from any branch in the chain, the first type of orientation predominates, although the bulk of the molecule is doubtless quite differently placed from that in figure 3, I; but, when the doublets are attached to a tertiary carbon, they appear

to be so screened that they cannot line up to any extent in the first orientation and the second predominates, making the dielectric constant and polarization abnormally low. Every intermediate condition may be represented. As the rigidity of the chain and hence the shape of the molecule depends upon the positions both of the hydroxyl group and of the branching of the chain, the relation of the orientation to the structural formula cannot be wholly explained as yet. It is hoped that investigation of these isomers in solution may throw more light upon the question.

It must be emphasized that the orientations discussed do not conform rigidly to one type or the other, that the extreme of one type may be so modified in some substances as to differ little from the other type, that both types may occur simultaneously, that very complex arrangements are not necessarily excluded, that the attraction of the dipoles may, in some cases, be so strong as to be virtually equivalent to secondary valence forces which cause the oriented molecules to be equivalent to polymers, and that, on the other hand, the interaction of the doublets may be so slight that the orientation is negligible. This flexible theory accounts for the abnormalities which are observed in many liquids and termed the result of molecular association, without the assumption of the formation of complex molecules to which chemical formulae are often assigned in a manner somewhat taxing to the imagination. Langmuir (21) in applying his theory of molecular surface energies to liquids has obtained satisfactory results on the assumption that a completely random orientation of the molecules exists. Smyth and Engel (50) have found, however, that while the effect of molecular orientation upon the vapor pressure of the liquid is negligible in many cases where the behavior of the polarization indicates the existence of orientation, the effect is appreciable in strongly polar liquids and so great in alcohols that the theory cannot apply in the simple form used by Langmuir. One must conclude that molecular orientation too slight to be apparent in its effect upon most physical properties of liquids may have a considerable effect upon the polarization.

STRUCTURE OF DERIVATIVES OF METHANE

The symmetrical tetrahedral structure commonly ascribed to methane should have no electric moment, but some evidence has been adduced to show that the molecule may be a pyramid with the carbon at the apex and the four hydrogens at the corners of a quadrilateral base. The carbon tetrachloride molecule is regarded as tetrahedral and the advocates of the pyramidal structure suppose that a tetra-substituted methane may be either tetrahedral or pyramidal (66). The absence of electric moment in $\text{C}(\text{NO}_2)_4$, CCl_4 , and $\text{C}(\text{CH}_2\text{Cl})_4$ (10) (69) is regarded as evidence that these structures are tetrahedral, while the presence of considerable moments in the molecules of $\text{C}(\text{OCH}_3)_4$, $\text{C}(\text{OC}_2\text{H}_5)_4$, and $\text{C}(\text{CH}_2\cdot\text{O}_2\text{C}\cdot\text{CH}_3)_4$ is supposed to show that they have the pyramidal structure (10) (66), which would almost certainly be electrically unsymmetrical and, therefore, possessed of a moment. However, in these latter compounds, as in the case of the ethers and alcohols, there are two doublets making an angle with one another at each oxygen. Since rotation is occurring around the bonds, as pointed out by Williams (69) and Höjendahl (14), the doublets would not at all times cancel one another and the average effect would result in a moment. A simple example of this effect of rotation is given by ethylene dichloride and ethylene glycol, which have large moments because of rotation about the C—C bond (46) (70). Therefore, as far as the evidence given by electric moments is concerned, some of the tetra-substituted methane molecules may be pyramidal in structure but are not necessarily so, while for others the pyramidal structure is highly improbable. As the evidence favoring the pyramidal structure for methane itself is of very doubtful character, and as it is highly improbable that the pyramidal structure would have the zero moment found by Sängner for methane, we are fairly secure in adhering to the generally accepted regular tetrahedron for the methane molecule.

Reference has already been made to the moment of the methyl chloride molecule. It may be considered that the replacement of a methane hydrogen by chlorine forms a doublet, the axis of which lies in the straight line between the carbon and chlorine nuclei,

that is, the line drawn from the center through an apex of the tetrahedron. The replacement of a second hydrogen by chlorine gives another similar doublet, the axis of which should make an angle of $109^{\circ} 28'$ with that of the first doublet if there were no distortion of the tetrahedral structure. The resultant moment of these two doublets should then be $2\mu \cos 54^{\circ} 44'$, where μ is the moment of the single doublet, that is, the moment of methylene

TABLE 5
Electric moments ($\times 10^{18}$) of certain halides and hydrocarbons

	X = Cl	Br	I
HX.....	1.03 (75)	0.79 (75)	0.38 (75)
CH ₃ X.....	1.59 (43a)		1.62 (29)
C ₂ H ₅ X.....	1.98 (43a)	1.86 (53)	1.66 (57)
C ₃ H ₇ X.....	1.89 (37)	1.87 (37)	
C ₂ H ₅ I.....		1.86 (37)	
C ₆ H ₅ X.....	1.52 (53)	1.5 (69)	
CH ₂ X ₂	1.6 (39)		
CHX ₃	1.05 (53)		
cis-CHX=CHX.....	1.85 (11)	1.22 (11)	0.75 (11)
trans-CHX=CHX.....	0 (11)	0 (11)	0 (11)
cis-CHCl=CHBr.....	1.54 (11)		
trans-CHCl=CHBr.....	0 (11)		
cis-CHCl=CHI.....		0.57 (12)	
trans-CHCl=CHI.....		1.27 (12)	
CH ₂ =CCl ₂	1.18 (11)		
CH ₂ =CH ₂	0 (54a)		
CH ₃ CH ₂ CH=CH ₂	0.37 (54a)		
CH=CH.....	0 (54a)		

chloride should be 1.155 times that of methyl chloride. The resultant of the three doublets in the chloroform molecule should be μ . Instead of being larger, the experimentally observed moment of methylene chloride is a little smaller than that of methyl chloride (table 5), because the mutual repulsion of the chlorine atoms pushes apart the negative ends of the two doublets, widening the angle between their axes and decreasing the resultant moment. In chloroform the repulsion of each of the chlorines by the other two is greater than that of the one chlorine by the other in methylene chloride, the spreading apart of the doublets is,

therefore, greater, and the resultant moment is so reduced as to be much smaller than that of methyl chloride.

The distortion of the molecule which shifts the positions of the electrical centers of gravity is shown by the moments of the hydrogen halides in table 5. As the infra-red absorption spectra show the distance of separation of the proton and the halogen nucleus to increase on passing from the chloride to the bromide to the iodide, one might expect the length and, therefore, the moment of the electric doublet to increase correspondingly. However, the reverse is true, for the binding forces on the electrons calculated from the refractions (48) decrease from chloride to bromide to iodide, thus making possible increased displacement of the electrons toward the hydrogen nuclei and shortening the distance between the positive and negative centers of gravity. In a similar fashion the moment of hydrogen sulphide is much lower than that of water (45) and the moment decreases on passing from ammonia to phosphine to arsine (64). The falling off in moment is much less pronounced in the alkyl halides, possibly because the attractive force upon the halogen electrons is less than that exerted by the proton which penetrates the halogen structure.

UNSATURATED BONDS

Electronic theories of valence have been applied very frequently to the double bond and, by many investigators, the double bond between two carbon atoms has been regarded as polar, one pair of electrons being shared between the two carbons and one of the carbons containing one more pair of electrons than the other. Smyth and Zahn (54a) have found the electric moment of the ethylene molecule to be zero, and have, therefore, concluded that no more than a small proportion of the ethylene molecules, if any, can be polar. Further, a molecule in which a single unpaired electron is held by each carbon might be expected to possess a moment and, if so, could not exist in any considerable quantity in ethylene. Support of this is given by the recent discovery of Vaidyanathan (62) that ethylene is diamagnetic instead of paramagnetic, as previously supposed, and should not, therefore, contain unpaired electrons. The zero moment found experi-

mentally for ethylene does not disprove the theory of Lowry (25) (26) and of Carothers (3) that a very small fraction of the molecules containing a double bond are polar at the bond and that it is this small fraction which is active. The small moment, 0.37×10^{-18} , found for α -butylene may be due to the difference in the electronegativities of the hydrogen on one side of the doubly-bonded carbons and the ethyl on the other side, as the electrons of the double bond are shown by the high refraction associated with them to be mobile and more easily displaceable than those in a single C—C bond.

If the double bond consisted essentially of a single electron pair held between the atoms and a second pair held by one atom or the other as supposed in most theories of a polar double bond, the difference in freedom of rotation between singly and doubly linked atoms would not be explained. This well recognized difficulty, which has been discussed by Sidgwick (42), is, of course, obvious in the problem of geometrical isomerism. The comparative rigidity of the double bond is brought out strikingly by the results of Errera for the moments of the acetylene dihalide molecules given in table 5, where the absence of moment in the *trans*-compound fits in admirably with the conventional representation of the double bond as formed by the sharing of an edge between two carbon tetrahedra. The doublets at the other imaginary tetrahedral apices thus brought into one plane would cancel one another in the *trans*-compounds so that the moments of the molecules would be 0. Any freedom of rotation about the bond would tend to produce electrical dissymmetry and a resultant moment, as found in ethylene chloride, bromide, and glycol (46) (70). One might wonder why the *cis*-compounds with the two halogen doublets reënforcing each other on the same side of the molecule do not have larger moments than the alkyl halides where there is only one halogen doublet. As was found in the chloromethanes and also in the dihalogenated benzenes, the two halogen atoms repel each other, widening the angle between the axes of their doublets and decreasing the resultant moment of the molecule as a whole. The repulsion and consequent widening of the angle should be greater, the larger the halogen atoms, and it is

evident that the moment is increasingly reduced on passing from chlorine to bromine to iodine. Purely geometrical considerations show that, when the two halogens are attached to the same tetrahedral carbon, the angle between their doublets is greater and the resultant moment less, as evidenced in the value for $\text{CH}_2=\text{CCl}_2$. Why the moment of $\text{CH}_2=\text{CCl}_2$ is lower than that of CH_2Cl_2 is not apparent. It may be due to some effect of the doublets upon the double bond. There is a similar difference between the approximate values calculated by Højendahl (14) for $\text{CH}_2=\text{CHBr}$ and CH_2Br . One might expect the moments of *cis*- and *trans*- $\text{CHCl}=\text{CHI}$ to bear somewhat the same relation to one another as those of *cis*- and *trans*- $\text{CHCl}=\text{CHBr}$, but the difference in electronegativity between the chlorine and iodine is apparently so great that the mobile electrons of the double bond are drawn much more strongly toward the chlorine and the electronic displacement in this direction is so great that the iodine becomes positive. Errera (12) supposes the positive end of the iodine doublet to lie toward the iodine while the negative end of the chlorine doublet is toward the chlorine. Thus, the doublets partly oppose each other and give a small moment in the *cis*-compound and partly support one another and give a larger moment in the *trans*-compound.

The rigidity of the double bond between carbon atoms is maintained in the structure proposed by Kharasch and Darkis (16) in which two pairs of electrons are shared between the two carbons, one pair being close to the carbon to which the less electronegative groups are attached and a definite polarity being postulated. This is neither proved nor disproved by the moments in table 5, but the zero moment found for ethylene shows the absence of any detectable polarity in this simple molecule, while the postulates of Kharasch and Darkis would lead us to expect a marked polarity. There appears to be no physical foundation for the postulate of Kharasch and Darkis that "the relative position of the second pair of valence electrons of the double bond depends upon the nature of radical attached to it in such a way that they are always on the carbon atom opposite to that carrying the most electronegative radicals." The more electronegative

radicals draw their binding electron pairs farther away from the carbon to which they are attached, thus increasing the effective nuclear charges of this carbon. The increased charge should tend to shift any other adjacent electrons toward this carbon and thus increase very slightly the effective nuclear charge of the carbon away from which they have shifted. A mechanism of this general character is commonly assumed to explain the transmission of an effect through a chain. The postulate of Kharasch and Darkis requires that the electrons be forced away from the carbon with the higher effective nuclear charge toward that with the lower charge. This would explain the somewhat doubtful differences observed between $\text{CH}_2=\text{CCl}_2$ and CH_2Cl_2 and between $\text{CH}_2=\text{CHBr}$ and CH_3Br , as, in the compounds containing the double bond, it would require a shift of electrons toward the carbons to which the halogens are not attached, which would decrease the moments. However effective such a postulate may be in explaining chemical behavior, it appears electrostatically unsound.

The triple bond in acetylene has been found to be electrically symmetrical (54a), the molecule having zero moment.

ELECTRICAL SYMMETRY OF THE PARAFFINS AND THE POLARITY OF SINGLE BONDS

The absence of electric moment found for the members of the paraffin series thus far studied must be considered in connection with the possible polarity of a single C—C bond and with the supposed difference in the electronegativities of alkyl radicals. The theory of alternating polarities has received much adverse criticism on chemical grounds, and the supposed physical evidence of alternation, given by melting points, heats of combustion, etc. has been shown to afford no proof of any intramolecular alternation of polarity (3) (16). The theory as proposed by Cuy (5) requires that, even in the paraffins, the carbons of the chain should be alternately positive and negative. The difference in polarity between the two carbons in ethane should give rise to an electric doublet, but no moment is found for the ethane molecule (54a). Although, because of the alternation and consequent cancelling

of the polarities, there should be no building up of large moments in the higher members of the series, there should certainly be moments in the molecules of many and differences should exist between adjacent members. *n*-Hexane and *n*-heptane have been shown to be without moment, as have also the other isomers of heptane and one octane (54). If any alternation in polarity occurred, it would be impossible that all of these molecules should be electrically symmetrical. Further evidence against an alternation in polarity is given by the absence of any difference in moment among the higher members of other homologous series to be considered presently.

The differences between the polarizations of the isomers of heptane were shown by Smyth and Stoops to be so small that the largest difference would, if due to but one pair of electrons, correspond to a displacement of the effective position of the charges of less than 3×10^{-11} cm. from a symmetrical location, that is, approximately .002 of the distance between the carbon nuclei in the chain. This distance was calculated as an upper limit for the displacement. Actually, such differences in polarization as were observed might easily occur without any lack of electric symmetry in the molecules. Hydrocarbon molecules may be resolved into various alkyl radicals to which it is customary to assign varying degrees of electronegativity. Thus, Lucas, Simpson and Carter (28) state that, in propane, due to the fact that hydrogen exerts a stronger pull on electrons than methyl does, the electron pairs joining the central carbon to hydrogens are presumably not so firmly held by the carbon, so that the polarities of all the carbon-hydrogen unions in propane are not the same, hydrogen joined to the secondary carbon being more negative than hydrogen joined to a primary carbon. If the carbon linkages are tetrahedrally arranged, this difference in the polarities would make the molecule electrically unsymmetrical. A greater effect should be produced at the central carbon of *n*-heptane, as the two propyl groups attached to it are supposed to be less electronegative than the methyl groups on the central carbon of propane, but *n*-heptane is found to possess no detectable moment. It is unnecessary to make any assumption of tetrahe-

dral linkages in order to conclude that the differently distributed groups in the isomers of heptane would give rise to electrical dissymmetry if their supposedly different electronegativities actually involved appreciably different displacements of their bonding electron pairs. The previously given calculation shows how small these displacements must be, if they exist at all. The electrical behavior of the paraffins thus gives no support to the hypothesis that the alkyl groups possess electronegativities which vary with the distance of the binding electron pair from the α -carbon.

TRANSMISSION OF INDUCED ELECTRONIC SHIFTS THROUGH A CARBON CHAIN

It would appear that the attachment of very strongly electronegative groups to the alkyl radicals should cause greater electron displacements and accentuate the differences between the radicals. When the hydroxyl is attached to an alkyl radical to form an alcohol, a strong electric moment results. In considering the dielectric constants of methyl, ethyl, and propyl alcohols, Thomson (61) has pointed out that the intense electric field due to the principal moment of the molecule might be expected to give rise by induction on the rest of the molecule to moments of the same sign as the original moment, thus increasing the moment of the molecule as a whole. The increase in the moment of the molecule due to these small moments resulting from electronic displacement would be greater, the greater the length of the carbon chain. What appeared to be evidence of such a small increase with increasing length of the carbon chain was obtained in calculating the moments of several alcohols and in other series as well (46), but, as previously pointed out, it seems probable that the apparent small increase in moment with increasing size of the molecule was due mainly to error caused by molecular association. The strong molecular association of the alcohols and water makes their moments difficult to determine with accuracy in the liquid state, but the most recent values (table 3) lie within 0.15×10^{-18} of 1.7×10^{-18} and show no regular variation with increase in the length of the chain. This, taken in conjunction with the very

small differences observed between the accurately determined values for the vapors of water, methyl alcohol, and ethyl alcohol, shows that there is no transmission of a measurable electronic shift through the carbon chain of the alcohol molecule and no electrostatic evidence of a difference in the electronegativities of the alkyl groups in the different alcohols.

Wolf and Lederle (73) have found that the electric moments of a number of ketones, including methyl hexyl ketone and methyl nonyl ketone, differ from the value for acetone by no more than the experimental error. Their results give no evidence of any change in moment with increasing length of the hydrocarbon chain. There is thus no measurable electrostatic effect transmitted beyond the first carbons attached to the carbonyl group and no sign of any alternating polarity in the chains, the evidence agreeing with that given by the alcohols.

In the molecules of the alkyl halides, the negative end of the electric doublet is toward the halogen. Consequently, the more electronegative the group attached to the halogen, that is, the more strongly it draws the binding electron pair toward itself, the shorter is the distance between the centers of gravity of the positive and negative electricity and the smaller the moment. This works out quite satisfactorily for hydrogen, methyl, and ethyl chlorides in which the moment increases as the supposed electronegativity decreases. The difference between ethyl chloride and butyl chloride is no greater than the combined probable errors in the values. An accurate value for methyl bromide is lacking, but approximate values calculated by Højendahl (14) indicate that the moment of methyl bromide is about 0.25×10^{-18} lower than that of ethyl bromide. The supposed differences in electronegativity of the bromides and iodides, as in the case of the chlorides, accord well with the increase in moment from hydrogen to ethyl. Beyond this, however, no difference is apparent in the chlorides and bromides, data for the iodides being lacking. The moments of chlorobenzene and bromobenzene are much higher than those of the corresponding hydrogen halides, although the phenyl group is supposed to be more electronegative than hydrogen. The supposedly different electronegativities are thus

only partially successful in explaining the differences in moment. It would appear that some effect is transmitted through the first two carbons of the chain in the halides, although the effect upon the second is small and, beyond the second, no effect is evident in the electric moment.

It is of interest to contrast this small or undetectable transmission of an electrical effect through a chain with the effect of the chain upon the ionization constants of unsubstituted and halogenated fatty acids (27). The constants for the unsubstituted acids show that, as in the case of the electric moments of the halides, lengthening of the hydrocarbon chain beyond two has little effect. The values for the halogenated acids are somewhat conflicting but, after a great drop in the effect upon the ionization when the halogen is moved from the first to the second carbon, the effect continues to diminish as the distance of the halogen from the carboxyl increases and is still noticeable in the δ -halogenated acid, where it has to be transmitted through five carbons and an oxygen. Yet, in the alkyl halides, no electronic shifts produced by halogen more than two carbons away can be detected by means of electric moments, and in the alcohols and ketones no induced shifts whatever are detected.

Our consideration of electric moments has shown that alkyl groups do not differ sufficiently in electronegativity to cause any detectable electrical dissymmetry in saturated hydrocarbons. When a halogen atom is attached to a carbon chain, only the first two carbons are apparently affected electrostatically, the β -carbon but slightly. It may be supposed that the shifts of electron pairs induced by the strongly electronegative halogen, or, putting it in other terms, by the large doublet at the end of the chain, are too small, in the carbons beyond the first two, to have any measurable electrostatic effect. Indeed, in view of the absence of any measurable induced electronic shifts in the chains of the alcohols and ketones, one may be skeptical of the differences in the halides as evidence of a general phenomenon. On the other hand, the ionization constants of the halogenated fatty acids show that the effect of a halogen is transmitted through five carbons and an oxygen. Moreover, the assumption of polarities

arising from the different electronegativities of radicals appears to be useful in explaining and predicting chemical behavior. It is difficult to believe that polarities as small as they must be, if they exist at all, in the chains of the alkyl groups or in a symmetrically located double bond can have powerful directive influence or greatly affect chemical activity or degree of ionization. The moments of any doublets existing must be so small that they would exert considerable forces only at very short distances and, at these distances, the interatomic forces which vary inversely as a high power of the distance should be so large that one might expect the effect of the forces due to the possible minute polarities to be negligible in comparison. In a molecule there is a possibility of a great variety of energy levels, many of which may differ from one another too little to give rise to measurable differences in polarity between molecules in which these levels are differently occupied. Too little is known of these levels in simple atoms to permit any certainty of reasoning in regard to complex compounds, but one cannot but wonder if the effects transmitted through long chains and the varied chemical behavior attributed to variation in polarity are not due to changes and differences in the energy levels occupied by the valence electrons.

CONCLUSIONS

The theory of Debye applies to gases and to dilute solutions in non-polar solvents and can be used to obtain the electric moments of molecules in the vapor state or in dilute solution. The effects of neighboring polar molecules upon one another cause deviations from the relations required by the Debye theory and these deviations may be used to study the orientation or possible association of the molecules. The deviation of various properties of liquids from normal behavior, which many investigators have attributed to the formation of molecular complexes of definite chemical formulae, may be explained in terms of mere orientation of the molecules relative to one another and of the electric forces acting between them. In extreme cases the orientation may become so pronounced and the forces so strong that definite complex molecules are formed. The tendency to orient

depends upon the shape of the molecule, upon the presence or absence of electric doublets in the molecule, upon the sizes and locations of the doublets and the directions of their axes, and, possibly, upon the nature of the molecular surfaces. The molecular arrangements are probably simple and very incomplete and more than one type of orientation may occur in the same liquid. The extent of the orientation, and even, in some cases, the type, varies with the temperature and the distance apart of the molecules.

The electric moment is shown to be the result of the electrically unsymmetrical distribution of electrons and nuclei in the molecule and, as such, to provide a means of studying molecular structure. The alcohols, ethers, and chloromethanes show how the moment of the molecule as a whole is the resultant of the moments of the doublets in the molecule, and how the directions of the axes of these doublets are altered by the steric effects of the atomic groups involved in the doublets. The moments of the acetylene dihalides give evidence of the absence of rotation about the double bond and show that, in these molecules, the atoms all lie in the same plane. The absence of electric moment in ethylene and acetylene shows the double and triple bonds to be essentially non-polar, although the small moment found for α -butylene indicates that the ease of displacement of the electrons in the double bond may give rise to some polarity when the bond is unsymmetrically located in the molecule.

The absence of moment in the paraffins gives no evidence of alternating polarities in the carbon chain or of any inherent dissymmetry in the electron linkages of alkyl radicals. The constancy of the moments in the series of the alcohols, ketones, and higher alkyl halides leads to the same conclusion and shows no transmission of a measurable polarity through the carbon chain except in the alkyl halides, where a difference in moment between the methyl and ethyl halides indicates a small effect in the second carbon, beyond which no effect is detected in the longer chains. The results suggest that the directive influences and effects upon chemical activity commonly attributed to differences in polarity may be due to differences in the energy levels occupied

by the valence electrons, which may or may not give rise to measurable polarity, and that polarity may occur as an accompanying result rather than as a determining factor in chemical behavior. Although pronounced polarity is doubtless a factor in chemical behavior, a large portion of the polarities assigned by the various electronic theories of valence must be regarded not as physical fact but merely as a pragmatic representation of chemical behavior.

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THE STRUCTURE OF MOLECULES AS REVEALED BY DIELECTRIC CONSTANT DATA

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There has been a tendency among American chemists to regard the electromagnetic properties of molecules as being of particular importance. Thus Langmuir (1) defines surface tension as a measure of the potential energy of the electromagnetic stray field which extends out from the surface layer of atoms. Harkins (2) speaks of an electromagnetic theory of surfaces and surface energy, and Lewis (3) finds little of value in the electrochemical viewpoint but elaborates a magnetochemical theory to account for the properties of molecules. On the other hand European scientists of the same period appear to have favored the electrostatic or electrochemical viewpoint. For example, Fraenkel (4) and Debye (5) have developed electrical theories of surface tension, the latter actually making considerable progress in calculating the magnitude of the surface tension in a number of cases; Guyot (6) and Frumkin (7) have studied the potential differences at interfaces for a considerable number of both aliphatic and aromatic compounds; and Debye (8) has successfully shown how one may have a dielectric constant, or rather a portion of it that varies with the absolute temperature if it be assumed that there exist permanent electrical dipoles in certain of the molecules. In recent years, with the impetus of results of dielectric constant studies such as are to be reported in this paper, the electrical nature of molecules seems again to be coming to the fore.

It would of course be desirable to be able to calculate the properties of molecules, inorganic as well as organic. We are certain that spatial considerations and calculations based on what the physicist calls classical mechanics are not fruitful. And

whether it will be possible to calculate the properties of any but the simplest "dumbbell" type of molecules by means of the Heisenberg quantum mechanics or the Schroedinger wave mechanics still remains to be seen. Therefore, it seemed practical to determine certain fundamental properties of the molecules from experimental data which are related to the actual electrical structure.

The property of the molecule chosen in the work I am to report to you was the electric moment.

There are, as far as the author is aware, but two methods for the accurate determination of the electric moment of a molecule:

1. A study of the temperature variation of the dielectric constant of the molecule in the gaseous condition.

2. A study of the dielectric constant and density data for suitable binary mixtures, that is, dilute solutions in which the solvent is of zero polarity and the solute is the molecule in question.

The data to be discussed in this article were, unless otherwise indicated, obtained by the second method. The dipole theory, and, in addition, the method of calculation of an electric moment has been given in a previous paper (9). Therefore, it is necessary for me simply to give the equations and to define the symbols as they will be used in the rest of the article. The equations are as follows:

$$P_{1,2} = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{f_1 M_1 + f_2 M_2}{d} = f_1 P_1 + f_2 P_2 \quad (1)$$

where $P_{1,2}$ = molar polarization of the solution

P_1 = molar polarization of the solvent

P_2 = molar polarization of the solute

f_1 = mole fraction of the solvent

f_2 = mole fraction of the solute

M_1 = molecular weight of the solvent

M_2 = molecular weight of the solute

d = density of the solution

ϵ = dielectric constant of the solution.

The quantity, P_2 is obtained from the equation

$$P_2 = \frac{(P_{1,2} - f_1 P_1)}{f_2} = P_2' + P_2'' \quad (2)$$

The assumption is made in this method of treatment that the polarization due to the non-polar solvent is always directly proportional to its mole fraction in solution. The molar polarization of the solute, P_2 , is obtained either by taking a tangent to the $P_{1,2}$ versus mole fraction of the solvent curve at the point where the mole fraction of the solvent is unity, and prolonging it until it cuts the axis where the mole fraction of the solute is unity, or by plotting a number of P_2 values obtained directly from equation (2) for dilute solutions and extrapolating the curve back to infinite dilution of the solute. In this manner the effect of a single solute molecule between the plates of the condenser is obtained, and effects which might be caused by an association of molecules are avoided. There must, of course, be no chemical reaction between solvent and solute.

In equation (2), P_2'' = polarization due to deformation of the molecule =

$$\frac{n_D^2 - 1}{n_D^2 + 2} \frac{M_2}{d'} \quad (3)$$

P_2' = polarization due to orientation of the molecule =

$$\frac{4}{3} \frac{\pi}{N} \frac{\mu^2}{kT} \quad (4)$$

where n_D = refractive index (D-line) for solute molecule

d' = density of solute molecule

N = Avogadro number = 6.06×10^{23}

μ = electric moment of the solute molecule

k = Boltzmann constant = 1.372×10^{-16}

T = Absolute temperature; in the work to be reported = 298° .

It will be evident that the polarization due to the deformation of the molecule cannot always be determined using the Lorentz-Lorenz formula at the temperature of the experiment; however, it is always possible to approximate this part of the total polarization in one of several ways, as follows:

1. By adding the individual atomic refractivities, making proper allowance for different types of linkages.

2. By determining the refractive index and density of the substance at some other temperature. (P_2'' is practically independent of state. Thus, for ethyl alcohol in the vapor state, $P_2'' = 13.2$ cc. and for ethyl alcohol in the liquid state, $P_2'' = 12.8$ cc.)

3. By following the suggestion of Errera that

$$P_2'' = \frac{\bar{\epsilon} - 1}{\bar{\epsilon} + 2} \frac{M_2}{\bar{d}},$$

where $\bar{\epsilon}$ and \bar{d} are the dielectric constant and density of the molecule in question in its solid state.

Having the total molar polarization of the solute molecule and that part of the polarization which is due to the deformation of the molecule, the part of the polarization due to the orientation of the molecule is readily obtained. The calculation of the electric moment follows directly from equation (4). The effect of any atomic polarization has been neglected in the results to follow, since it is generally of the order of magnitude of the error in P_2'' , and is without significance for the work to be discussed in this article.

One might expect that the electric moment of a molecule determined in different non-polar solvents might vary somewhat, since the dielectric constant of the solvent changes. It may be said, however, that within the limits of the experimental error of a series of determinations for which all the precautions of precision measurements were taken, such is not the case. In other words the molar polarization, and therefore the electric moment of a solute molecule, is independent of the non-polar solvent used. This fact is illustrated in table 1 (9).

The purpose of this paper is two-fold:

I. To discuss the use of electric moment data in giving information concerning the structure of molecules.

II. To discuss the relation between the results of these studies and certain other well-known phenomena of physics and physical chemistry.

PART I

The material to be treated in this part has been divided into the following sections:

- a. Mono-, di-, and tri-substituted benzenes.
- b. Derivatives of diphenyl.
- c. Derivatives of methane in which all four valences are satisfied by like atoms or groups of atoms. Type $C\alpha_4$.
- d. Typical inorganic molecules.

The data to be used in the discussion are, with few exceptions, those of the author and his collaborators (10) and are presented in table 2. Where other data are used in the text they will be introduced with suitable references.

TABLE 1
Polarization in non-polar solvents

MOLECULE	P_1	P_1'	P_2'	$\mu \times 10^{18}$
Solvent: benzene ($\epsilon = 2.280$)				
Nitrobenzene	348.0	32.0	316.0	3.90
Chlorobenzene	82.0	31.0	51.0	1.52
Phenol.	89.0	27.5	61.5	1.70
Solvent: carbon disulphide ($\epsilon = 2.633$)				
Nitrobenzene	346.0	32.0	314.0	3.89
Chlorobenzene	82.5	31.0	51.5	1.52
Phenol.	83.6	27.5	56.1	1.64
Naphthalene	54.0	43.5	10.5	0.69
Solvent: hexane ($\epsilon = 1.904$)				
Nitrobenzene	346.0	32.0	314.0	3.89
Chlorobenzene	84.0	31.0	53.0	1.55
Naphthalene.	55.0	43.5	11.5	0.72

a. Mono-, di-, and tri-substituted benzenes

Benzene itself is a typical non-polar molecule, but when one of its hydrogen atoms is replaced by any other atom or by a group of atoms a polar molecule will be formed. Thus, the introduction of a chlorine atom, a methyl group, a hydroxyl group, etc., will cause the formation of a molecule whose polarity is quantitatively measured by the magnitude of its electric moment. Sufficient electric moment data are now available to indicate

TABLE 2

Electric moments of some derivatives of benzene, diphenyl and methane, and also of some typical inorganic molecules

MOLECULE	P ₁	P ₁ *	P ₁ '	$\mu \times 10^{18}$
Solvent: benzene (25°C)				
Toluene.....	36.3	30.3	6.0	0.52
<i>o</i> -Xylene.....	40.8	35.0	5.8	0.52
<i>p</i> -Xylene.....	36.7	35.5	1.2	0.06
<i>o</i> -Dinitrobenzene.....	800	35	765	6.05
<i>m</i> -Dinitrobenzene.....	338	35	303	3.81
<i>p</i> -Dinitrobenzene.....	37.0	34	3	0.32
1,3,5-Trinitrobenzene.....	55.0	40	15.0	0.80
<i>o</i> -Nitrotoluene.....	331	38	293	3.75
<i>m</i> -Nitrotoluene.....	407	38	369	4.20
<i>p</i> -Nitrotoluene.....	463	38	425	4.50
Benzoic acid.....	43.5	24.6	18.9	1.0
Bromobenzene.....	82	33	49	1.5
Benzaldehyde.....	190	35	155	2.75
<i>p</i> -Nitrobenzaldehyde.....	158	38	120	2.4
<i>p</i> -Nitrobenzoic acid.....	300	40	260	3.5
<i>p</i> -Chlorobromobenzene.....	40	39	1	0.2
<i>o</i> -Cresyl methyl ether.....	57	37	20	1.0
<i>m</i> -Cresyl methyl ether.....	65	37	28	1.17
<i>p</i> -Cresyl methyl ether.....	68	37	31	1.20
<i>o</i> -Cresol.....	74	32	42	1.44
<i>m</i> -Cresol.....	84	32	52	1.60
<i>p</i> -Cresol.....	87	32	55	1.64
<i>o</i> -Chlorophenol.....	68	34	34	1.3
<i>m</i> -Chlorophenol.....	130	34	96	2.17
<i>p</i> -Chlorophenol.....	148	34	114	2.4
<i>o</i> -Nitrophenol.....	235	33	202	3.1
<i>m</i> -Nitrophenol.....	348	33	315	3.9
<i>p</i> -Nitrophenol.....	563	33	530	5.05
<i>p</i> -Phenylenediamine*.....	45	35	10	0.7
Hydroquinone diethyl ether.....	116	50	65	1.7
Hydroquinone diacetate.....	150	50	100	2.2
Terephthalic acid dimethyl ester.....	152	50	102	2.2
Mesitylene.....	42	41	1	0.2
1,3,5-Triethylbenzene.....	56	55	1	0.2
Phloroglucinol trimethyl ether.....	130	55	75	1.8
Phloroglucinol triacetate.....	185	65	120	2.4
Diphenyl.....	50	50	0	0
4,4'-Dichlorodiphenyl.....	63	63	0	0
4,4'-Dinitrodiphenyl.....	65	65	0	0
4,4'-Diaminodiphenyl.....	100	60	40	1.3

TABLE 2—*Concluded*

MOLECULE	P_1	P_1^*	P_1'	$\mu \times 10^{18}$
Solvent: benzene (25°C)— <i>Concluded</i>				
4,4'-Diethoxydiphenyl	150	75	75	1.9
4,4'-Diacetylphenyl.....	155	80	75	1.9
Hexane.....	30.5	29.6	0.9	0.05
Carbon disulphide.	22.2	21.1	1.1	0.06
Chloroform.....	47.5	21.3	26.2	1.10
Carbon tetrachloride	28.2	28.3	0	0
Ethyl ether	54.5	23.0	31.5	1.22
Iodine.....	60.2	28.0	32.2	1.2
Stannic iodide.	26.7	30	0	0
Silver perchlorate	477.0	16	461.0	4.7
Water.....	64	4	60	1.7
Antimony triiodide	80	76	4	0.4
Tetranitromethane.....	32.5	31	1.5	0.2
Pentaerythritol tetrabromide	56	56	0	0
Pentaerythritol tetraacetate.....	140	70	70	1.9
Solvent: carbon tetrachloride				
Benzene.....	26.7	25.8	0.9	0.06
Toluene.....	33.7	30.3	3.4	0.40
Chloroform.....	49.8	21.3	28.5	1.15
Ethyl ether.....	56.0	23.0	33.0	1.24
Methyl acetate	78.0	18.0	60.0	1.67
Ethyl acetate.....	87.0	22.2	64.8	1.74
Acetone.....	170.0	16.0	154.0	2.70
Ethyl alcohol.....	73.5	16.0	57.5	1.63
Isoamyl alcohol.....	86.0	13.0	73.0	1.85

* Redetermination of the electric moment of this molecule gives a value slightly higher than that originally reported (J. Am. Chem. Soc. 50, 2332 (1928)). The substance is so difficultly soluble in benzene that an exact determination is impossible with the apparatus now available. The value given, however, must be approximately correct. Thus, the original conclusion with regard to the structure of the benzidine molecule is unchanged.

that an atom or group of atoms when introduced into a molecule may be considered as an electrical vector, having both magnitude and direction. The idea to be conveyed here is that each atom or group is characterized by a more or less definite moment, and not that each will always necessarily produce exactly the same

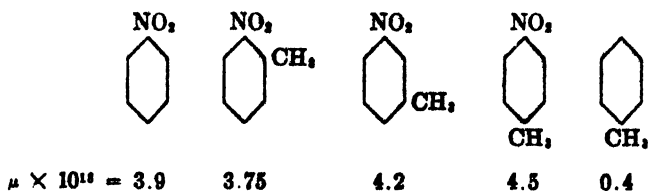
moment when introduced into methane, ethane, benzene, or a hydrogen molecule. This is evident from table 3.

Thus, the introduction of an OH group into methane, benzene and hydrogen gives a moment of magnitude, $\mu = 1.65 \times 10^{-18}$ e.s.u., and the introduction of an NH₂ group into benzene and hydrogen gives a moment of magnitude, $\mu = 1.5 \times 10^{-18}$ e.s.u. This agreement is, however, probably due to internal compensations. There are many ways in which the vector value of the group may be altered, since when such an atom or group is introduced the number of electrons present in the molecule is changed.

TABLE 3
Substitution of atoms in non-polar molecules

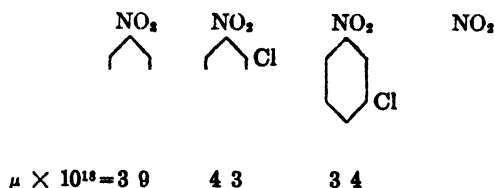
ATOM OR GROUP	ELECTRIC MOMENT $\times 10^{18}$		
	For C ₆ H ₅ X	For CH ₃ X	For HX
Cl.....	1.52	2.0 (14)	1.04 (11)
Br.....	1.51	1.86	0.79 (11)
I.....		1.6	0.38 (11)
CN.....	3.85	3.4	
OH.....	1.65	1.64	1.7
NO ₂	3.9	3.1 (12)	
NH ₂	1.5		1.53 (13)

When two of these groups are substituted in benzene, the second in various positions with respect to the first, it is possible to assign an electrical character to each of these groups, the only limitation being that one of the groups must be used as a reference. The table to be presented was formed making the assumption that the methyl group is positive in nature. From the data for the nitrotoluenes it will be evident that if the CH₃ group has a positive character, the NO₂ group must have a negative character.




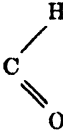

The moment of the nitrotoluene molecule steadily increases as the CH_3 group moves from the *ortho*, through the *meta*, to the *para* position.

The data for the chloronitrobenzenes, taken from Højendahl (12), illustrate the fact that the Cl atom and NO_2 group exert like electrical effects, since as the Cl atom moves from the *ortho*, through the *meta*, to the *para* position the moment steadily decreases.



In this manner charges and approximate values have been assigned to certain atoms and groups. These are given in table 4.

TABLE 4
Characteristic moments of atoms or groups

GROUP	MOMENT	GROUP	MOMENT
NO_2	-3.9		-0.9
	-2.8		+0.4
OH	-1.7	CH_3	+1.5
Cl	-1.5	NH_2	
Br	-1.5		

Assuming for the present that we are dealing with a benzene molecule in which the six carbon atoms are found in a single plane, one might assume that the vectors characteristic of the various atoms or groups would also act in this plane. It is probable that in the case of the substitution of a single atom and in the case of certain very simple groups, this assumption will not lead to any particular difficulty, but the author wishes emphatically to point out that in general this assumption may

not be made. These statements are of interest in connection with an article by Thomson (15), written before data such as are given in this paper were available. Thomson makes essentially the same assumption that is noted above in the statement, "neglecting the deflection of the two doublets due to their action on each other," which precedes the equations given to calculate the moment of disubstituted benzenes. These equations or their equivalents have been used by Höjendahl (16) to treat the data for the various chloronitrobenzenes and dinitrobenzenes and by Smyth and Morgan (17) to treat the data for the dichloro-

TABLE 5
Electric moment data for disubstituted benzenes

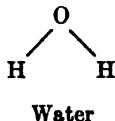
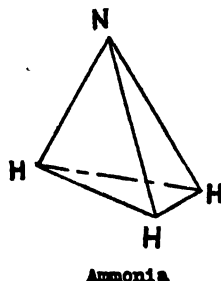
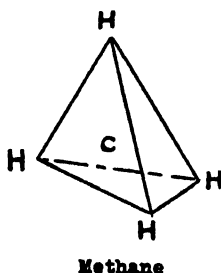
MOLECULE	OBSERVED MOMENT	CALCULATED MOMENT
$ \begin{array}{c} \text{H} \\ \diagup \\ p\text{-NO}_2\text{C}_6\text{H}_4\text{C} \\ \parallel \\ \text{O} \\ \parallel \\ \text{O} \\ \diagdown \\ \text{OH} \end{array} $	2.4×10^{-18}	1.1×10^{-18}
$ \begin{array}{c} \text{H} \\ \diagup \\ p\text{-NO}_2\text{C}_6\text{H}_4\text{C} \\ \parallel \\ \text{O} \\ \parallel \\ \text{O} \\ \diagdown \\ \text{OH} \end{array} $	3.5×10^{-18}	3.0×10^{-18}
$p\text{-NO}_2\text{C}_6\text{H}_4\text{NH}_2$	7.1×10^{-18}	5.4×10^{-18}
$p\text{-ClC}_6\text{H}_4\text{OH}$	2.4×10^{-18}	0.2×10^{-18}
$p\text{-NO}_2\text{C}_6\text{H}_4\text{OH}$	5.1×10^{-18}	2.2×10^{-18}

benzenes and cresols. The data for the dichlorobenzenes, chloronitrobenzenes, and dinitrobenzenes could be treated in this manner because only atoms and simple groups are involved, but in the case of the cresols it was necessary to assume values for the CH_3 and OH groups which are hard to justify experimentally. The reason why these simple equations cannot be used in the case of the cresols appears to be that the stereochemistry of the oxygen atom of the hydroxyl group was not taken into account.

Further evidence that the assumption of vectors acting in the plane of the benzene ring is untenable is presented in table 5.

The conclusion to be drawn from these data is that in the case

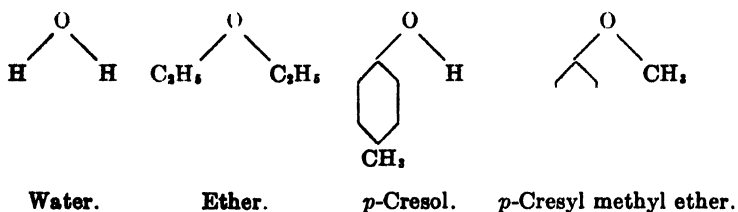
of $\text{C} \begin{smallmatrix} \text{H} \\ \diagup \\ \text{O} \end{smallmatrix}$, $\text{C} \begin{smallmatrix} \text{O} \\ \diagup \\ \text{OH} \end{smallmatrix}$, NH_2 and OH groups the vector is directed in space rather than in the plane of the benzene ring, due to the fact that it is joined to the benzene nucleus by a carbon, nitrogen or oxygen atom. The structure for the methane, ammonia, and water molecules has been worked out in more or less detail (18) and may be represented by the following diagrams:



This indicates that atoms and groups replacing the hydrogen atoms will be projected into space rather than in a plane; in the case under discussion, the plane of the benzene nucleus. Höjendahl (12) has termed such groups as those just mentioned "inclined" groups. Inclined groups must of course be in the great majority in chemistry.

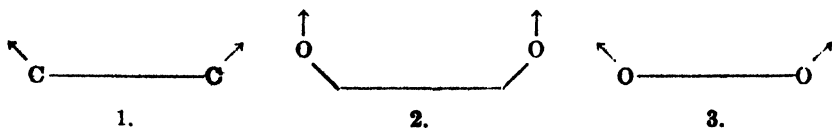
The writer has studied the stereochemistry of the oxygen atom by considering the effect of the substitution of several simple atoms or groups into the various positions in phenol. It is immediately evident that these compounds cannot be treated as derivatives of benzene in the simple sense referred to above (15). It has been pointed out (19) that the values obtained for the cresols and cresyl methyl ethers may best be accounted for by assuming that these compounds have a structure similar to that which has been proved for water and to that which has been

assumed for the ethers. These different structures may be represented schematically as follows:



The electric moments for the chlorophenols and nitrophenols have been taken from unpublished data of Mr. Fogelberg, working with the writer at the University of Wisconsin. A glance at the results for these molecules, which have also been included in table 2, will show that the electric moment increases sharply when the hydroxyl group is moved from the *ortho*, through the *meta* to the *para* position. According to the equations of Thomson (15), based on the consideration of a simple benzene formula and a vector representation of the polarity of the substituent groups, the value should decrease sharply, in fact, in the case of *p*-chlorophenol, the electric moment should practically vanish. It is possible to account for the experimentally determined values when a structure similar to water and ether is assumed. A careful study of the infra-red absorption bands for these various substituted phenols should enable one to determine whether or not this structure is the correct one.

The data for certain like *para* di-substituted benzenes are of considerable interest because they also show the effect of the inclination of groups and interactions between them. According to the equations of Thomson, all like *para* di-substituted benzenes should have a zero moment. Reference to table 2 will show that in the cases of (1) the dimethyl ester of terephthalic acid, (2) hydroquinone diacetate, and (3) hydroquinone diethyl ether such is far from the truth. These molecules must have a structure similar to that indicated in the following diagrams



It is probable, also, that the structure of hydroquinone should be given by one of these formulas. In the case of the derivatives of hydroquinone there is as yet no means of differentiating between formulas No. 2 and No. 3. The study of potential differences at interfaces has led Frumkin (20) to favor formula No. 3. At any rate the data for these compounds show clearly that the stereochemistry of the atom joined to the benzene nucleus, in this case, carbon and oxygen, respectively, must be considered.

It may be said from studies such as are reported in this article that both the carbon and oxygen atoms are tetrahedral in nature. It will be evident, also, that when the few data necessary become available the stereochemical properties of a number of other atoms may be worked out in some detail.

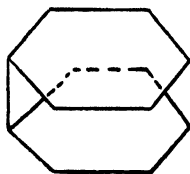
In connection with the discussion of these *para* substituted dioxybenzenes the writer would like to call attention to the fact that these results are *not* in contradiction to what one should expect on the basis of the classical stereochemistry, although this interpretation has been placed upon them by Ebert, Eisenschitz and v. Hartel (21). As has been pointed out, it is exactly this stereochemistry which would lead one to expect the results which have actually been found to exist.

The data for the symmetrical tri-substituted derivatives of benzene lead to definite conclusions concerning the structure of the benzene nucleus. If any of the formulas proposed by Körner (22), Baeyer (23), and Ladenburg (24) are correct, a finite electric moment for *every* like tri-substituted compound of the symmetrical type should result. The evidence is conclusive in the case of mesitylene and 1,3,5-triethylbenzene (see table 2) and in the case of 1,3,5-tribromobenzene (12) that no such moment results, a fact which clearly and definitely indicates that the six carbon atoms in the benzene nucleus lie in a single plane.

In the same way that it is possible for a like *para* disubstituted derivative of benzene to have a finite moment, it is also possible to have a like 1,3,5-trisubstituted derivative of benzene which will show a finite moment. The presence of a finite moment in the case of the two derivatives of phloroglucinol is indicated in the data of table 2.

b. Derivatives of diphenyl

A study of the chemical properties of diphenyl and its derivatives has led to interesting speculations concerning the structures of the various molecules. Adkins, Steinbring and Pickering (25), as a result of their chemical studies, conclude that the non-formation of the anhydrides is due to the fact that in the dinitro and dihydroxy acids the rings are extended as in the conventional formula, while in the amino or benzidine type of acids the rings are superimposed. Kuhn and Albrecht (26), discussing the same question, "come to the conclusion that it is not possible to explain diphenyl and its derivatives by means of a single space formula." In the case of the *p,p'*-disubstituted diphenyl compounds, two types of formula are discussed, as follows: (1) A formula in which the axes of the two benzene rings lie in a straight line; (2) A formula in which the axes of the two benzene rings make an angle with each other *or* are directed parallel to each other, as indicated in the following diagram.

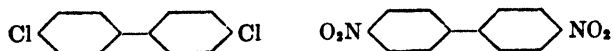


In the discussion of the results of electric moment studies for the various derivatives of diphenyl, it is necessary to consider the data not only for the particular derivatives of diphenyl but also for the corresponding derivatives of benzene. These data, with the exception of the value of the electric moment for *p*-dichlorobenzene which has been given by Smyth and Morgan (17) are given in table 2.

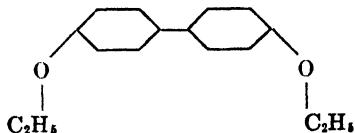
With regard to the structure of the several derivatives of diphenyl, the following statements may be made.

(1) Since the electric moments of the compounds *p*-dichlorobenzene and 4,4'-dichlorodiphenyl, and of *p*-dinitrobenzene and 4,4'-dinitrodiphenyl, are zero, and since the introduction of a single Cl atom or NO₂ group into the benzene nucleus causes

a highly unsymmetrical molecule, the conclusion is definite that in the case of the compounds, 4,4'-dichlorodiphenyl and 4,4'-dinitrodiphenyl the rings of the diphenyl nucleus are co-axial. They are represented diagrammatically in the following sketches.



(2) The electric moments of the compounds hydroquinone diethyl ether and 4,4'-diethoxydiphenyl (1.7 and 1.9×10^{-18} e.s.u., respectively) must be considered to be of the same order of magnitude. The reason why hydroquinone diethyl ether gives a finite moment has been discussed above. Since the magnitude of the moment of the corresponding diphenyl derivative is the same, it is highly probable that its structure is similar. The conclusion to be drawn from these considerations is, again, that the benzene rings are extended. This structure is suggested in the following diagram.



In this connection it may be pointed out that until more accurate experiments are available for this and similar substances, the possibility of a slight deformation from the extended position is not excluded.

(3) The electric moment data for the compounds *p*-phenylenediamine and 4,4'-diaminodiphenyl distinctly indicate a collapsed or perhaps folded structure for the latter substance, at least in benzene solution (27). The electric moment of the similar benzene derivative is small; thus there is only a slight tendency for the NH_2 groups to be bent from the plane of the benzene ring. 4,4'-Diaminodiphenyl has a comparatively large moment, $\mu = 1.3 \times 10^{-18}$ e.s.u. If the benzene rings of the diphenyl were extended, as has been shown to be the case for the dichloro-, dinitro- and diethoxy-derivatives, there can be little question that a much smaller moment would have resulted for the benzidine molecule as well.

Thus the electric moment data indicate the truth of the statement quoted above from the article of Adkins, Steinbring and Pickering, namely, that in the dinitro- and dihydroxy-derivatives of diphenyl the rings are extended as in the conventional formula, while in the amino or benzidine type the rings are folded. They are also in accord with the conclusions of Kuhn and Albrecht. It is evident, however, that these data are as yet insufficient to establish the general truth of these conclusions.

c. Derivatives of methane of type $C\alpha_4$

There are found in table 2 data for but four derivatives of methane of the type $C\alpha_4$. Electric moment data for molecules

TABLE 6
Electric moment data for molecules of type $C\alpha_4$

MOLECULE	FINITE ELECTRIC MOMENT
$C(OCH_3)_4$	Present
$C(OC_2H_5)_4$	Present
$C(CH_2Cl)_4$	Absent
$C(CH_2OOCCH_3)_4$	Present
$C(COOCH_3)_4$	Present
$C(COOC_2H_5)_4$	Present
CCl_4	Absent

of this type are of great significance because of the structural considerations involved, and to properly discuss the point it will be necessary to introduce certain of the more numerous data of Ebert, Eisenschitz and v. Hartel (21) as well.

Until within recent years scientists had been satisfied with the classical idea of the tetrahedral carbon atom in spite of the fact that there could be no real evidence in its favor. When x-ray methods for the determination of the structure of matter were made available, it became important to show that the tetrahedral carbon atom actually did exist. This was readily accomplished. The question then arose as to whether or not the carbon atom might not also show different stereochemical properties from that of the tetrahedron, and it appeared, to certain investigators at

least, that such was actually the case. For our present purpose it is necessary to mention only the papers on this subject by Weissenberg (28) in which it was claimed that polar molecules of the type $C\alpha_4$ possessed the symmetry of a pyramid instead of that of a tetrahedron.

The electric moment data for this type of compound may be conveniently divided into two classes; (1) those molecules whose electric moment is zero, and (2) those molecules which possess a finite electric moment. Concerning the interpretation of the results for the molecules of the first group, there can be no question. The four valences of the central carbon atom are directed toward the corners of a regular tetrahedron.

To account for the presence of a dipole moment in the case of molecules of the second group, two explanations have been given. The first, due to Ebert, Eisenschitz and v. Hartel (21) and to Weissenberg (28), assumes that the four valences of the central carbon atom are directed toward the corners of a regular pyramid. It can readily be seen that if the carbon atom may assume this form and the four valences are satisfied by like groups, a molecule possessing a finite dipole moment must result. This explanation denies the existence of the classical tetrahedral carbon atom in these particular cases.

The second explanation has been given by the writer (29) and by Höjendahl (12). It retains the idea of the tetrahedral carbon atom and accounts for the asymmetric properties of molecules of the second class now under discussion, as being caused by the stereochemistry of the groups which satisfy the four valences of the carbon atom and by the interaction between these groups as their lengths and complexities are increased. It may be pointed out that in every case of a molecule of the type $C\alpha_4$ known to date which has a finite moment there is an oxygen atom in each group, either attached directly to, or very close to, the central carbon atom. The effect of the presence of an oxygen atom in the various phenols and dioxy- and trioxybenzenes has been discussed at some length, and it is only reasonable to suppose that where such an atom is present in the part of each group directly attached to the central carbon atom of a molecule of

the type $C\alpha_4$ a similar asymmetry may be introduced. Thus, such a molecule may have a tetrahedral central carbon atom and still be asymmetrical as a whole because the groups attached to the central atom are bent from the directions of the valences of the central tetrahedral carbon atom. In spite of the fact that Ebert, Eisenschitz and v. Hartel (21) do not calculate the exact dipole moments of their various compounds, a careful inspection of their data shows that as the length and complexity of the substituent group increases, the polarity of the molecule increases strongly. It would seem if the explanation of the pyramidal carbon atom were the correct one that an increase in the length of hydrocarbon chain would have little or no effect on the polarity of the molecule, as has actually been shown to be the case for the simple aliphatic alcohols and ketones. The data for $C(OCH_3)_4$, $\mu = 0.7 \times 10^{-18}$ e.s.u., and $C(OC_2H_5)_4$, $\mu = 1.1 \times 10^{-18}$ e.s.u., calculated from the polarization values given by Ebert, Eisenschitz and v. Hartel, show a distinct increase in polarity as the complexity of the molecule changes but slightly.

Further evidence for the explanation which retains the tetrahedral carbon atom and ascribes the polar properties of this class of molecules to properties of the substituent groups is to be found in the study of the surface properties of the molecule pentaerythritol tetrapalmitate reported by Adam (30). The cross-sectional area of this molecule was found to be 100×10^{-16} sq. cm., but was easily reducible by compression to 80×10^{-16} sq. cm., or almost exactly four times the cross-sectional area of a single closely packed hydrocarbon chain. The conclusion drawn by Adam was that the four chains (substituent groups) must lie parallel, two of them having been bent back through a large angle. Thus the four substituent groups are easily pliable and interactions between them could produce asymmetry in the molecule. This molecule differs from pentaerythritol tetraacetate, for which electric moment data are given by both Ebert and his co-workers (21) and in table 2, only by the lengths of the hydrocarbon chains.

To summarize, it may be pointed out that electric moment data for molecules of the types $1,4-C_6H_4\alpha_2$, $1,3,5-C_6H_3\alpha_3$, and $C\alpha_4$ are now available which indicate that in the case of very

simple substituents, a symmetrical molecule is formed, but that as the substituents become more and more complex, asymmetrical molecules result. Complexity in groups seems in general to be caused by the presence of such atoms as oxygen (and it may be predicted that such atoms as sulphur, nitrogen, phosphorus and others will produce similar effects), which have definite spatial configurations, and by interactions between groups as their length and shapes change. The presence of finite dipole moments in molecules of these types need not disturb in any way our feeling for the simple configuration of the benzene nucleus with the six carbon atoms lying in a single plane, and the tetrahedral model of classical stereochemistry for the methane molecule.

d. Typical inorganic molecules

It might be predicted that the method which has been used to determine the electric moment of the molecules discussed to this point could not be used to determine the moments of inorganic molecules. This method, it will be recalled, depends upon a study of dielectric constant and density data for dilute solutions in which the solvent is non-polar in character. Such is, however, not the case, although it is true that there have been comparatively few such measurements made because the present experimental difficulties are greater. Inorganic molecules are generally but slightly soluble in such solvents as benzene, hexane, and carbon tetrachloride, but it is not at all impossible that other non-polar solvents which will dissolve this type of molecule can be found.

The value obtained for the water molecule from dielectric constant and density data for a saturated solution of water in benzene (31), $\mu = 1.7 \times 10^{-18}$ e.s.u., must probably be considered to be slightly in error because Sanger and Steiger (32), in a very careful and painstaking research, have obtained the value, $\mu = 1.85 \times 10^{-18}$ e.s.u., from a study of the temperature variation of the dielectric constant of water vapor. The accuracy of the result obtained from dielectric constant and density data for solutions depends very considerably upon the exactness with which the concentration of the solute in solution is known. In

this particular case, since water is but difficultly soluble in benzene, it is extremely difficult to determine the solubility of water in benzene with a degree of accuracy sufficient for the purpose. The value used in the calculation was that of Hill (33), a value in good agreement with values which had previously been reported by Groschuff (34) and by Richards, Carver and Schumb (35). It is of interest that after this value was reported the results of a new solubility determination were communicated to the author, these results changing the value for the electric moment of water to 1.87×10^{-18} e.s.u., that is, practically the identical result of Sanger and Steiger.

The result for stannic iodide, $\mu = 0$, indicates that it has a structure similar to that which has been proposed for methane. The four iodine atoms are attached to the four valences of the tin atom at the corners of a regular tetrahedron. Thus it appears that the tetrahedral arrangement for atoms at the center of the periodic table (carbon, silicon, germanium, tin) is quite common.

Antimony triiodide appears to have a very small electric moment. In the series NH_3 , $\mu = 1.5 \times 10^{-18}$ e.s.u., PH_3 , $\mu = 0.5 \times 10^{-18}$ e.s.u., and AsH_3 , $\mu = 0.15 \times 10^{-18}$ e.s.u., studied by Watson (36) it is apparent that as the size of an atom in any given group in the periodic table increases, the moment of any simple molecule in which this atom appears will decrease. This effect is also evident in the data for the halogen acids due to Zahn which have been presented in table 3, and in other data, and appears to be a quite general phenomenon. It is highly probable that all the atoms of Group V (nitrogen, phosphorus, arsenic, antimony) have their valences directed as shown in the diagram for ammonia which has previously been given.

Again, the electric moment for hydrogen sulphide, $\mu = 1.1 \times 10^{-18}$ e.s.u. (37), is considerably smaller than the moment of the water molecule, and it may be predicted that the moment for hydrogen selenide will be even smaller.

As yet there are but few data available for compounds of the metals of the first and second groups with strongly electronegative atoms or groups of atoms. The result for silver perchlorate, measured in benzene solution and given in table 2,

indicates that these molecules will have a very high polarity. Thus, molecules formed by the atoms near the middle of the table are much less polar in character than those formed by the strongly electro-positive (and strongly electro-negative) groups; further, those molecules formed by atoms with the larger radii will be less polar than those formed by atoms with the smaller radii.

Therefore, in spite of the fact that so few data are as yet available, it seems possible to conclude that there is no abrupt transition between what have been termed homopolar and heteropolar linkages in molecules.

PART II.

The material to be treated in this part shows the relation between the results of dielectric constant studies and

- a. X-ray analysis.
- b. Adsorbed film data.
- c. Association.
- d. Compound formation.

a. X-ray analysis

At first thought it might appear that it should always be possible to compare the results of such studies as have been described above, that is, data concerning the structure of molecules in the dissolved state, with their structure in the solid state as determined by x-ray analysis. A comparison of the results of both methods is now possible in a few cases, and it appears quite definitely that one may not assume that simply because a molecule is symmetrically built in the solid state it must also be symmetrical in the dissolved state, and vice versa. Indeed, this is not a surprising result when the nature of the forces operative in the case of a crystal is compared with the nature of the forces which would be expected in the case of a liquid or dissolved substance.

As examples of molecules in which the atoms are simply and symmetrically arranged about a central atom in both the solid and dissolved states, one may mention stannic iodide and carbon

dioxide. The case of carbon dioxide is extremely interesting, because although the results of x-ray studies (38) have indicated without any question a linear and symmetrical arrangement of the three atoms which make up the molecule, it was thought that the molecule possessed a finite electric moment which would indicate a triangular arrangement of the atoms. Data for the infra-red absorption bands for carbon dioxide have led to both conclusions (39). Recently its electric moment has been re-determined by Stuart (40) who gives as his result the value, $\mu = 0$. The experimental work was carefully done, and it appears definitely that carbon dioxide has a zero moment. The temperature coefficient of the dielectric constant of the vapor was studied in this research. The three atoms must, therefore, have a linear and symmetrical arrangement in the gas phase as well as in the solid form.

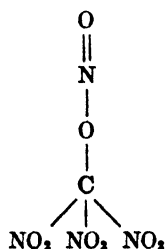
The derivatives of methane of the type $C\alpha_4$ were studied in order to compare the results with those obtained from x-ray determinations. At the time the work was started there was considerable discussion about the structure of pentaerythritol, $C(CH_2OH)_4$. The early interpretations of the x-ray diagrams, due to Mark and Weissenberg (41) and to Huggins and Hendricks (42), appeared to indicate a structure in which the four carbon atoms attached to the central carbon atom were located in a plane. If this were correct, then one should expect that pentaerythritol, and perhaps also its simple halogen derivatives, $C(CH_2Cl)_4$ and $C(CH_2Br)_4$, should have finite electric moments. It is quite impossible to dissolve pentaerythritol in sufficient quantity in any of the non-polar solvents now commonly used for electric moment determinations, so that there are as yet no data available for this substance. The derivatives $C(CH_2Cl)_4$ and $C(CH_2Br)_4$ gave zero moments, indicating a tetrahedral rather than a pyramidal arrangement of groups about the central carbon atom. This does not mean, however, that pentaerythritol itself must have a zero moment; indeed, like hydroquinone and phloroglucinol, it probably has a small but finite moment.

By this time considerable curiosity had been aroused in this apparently new type of carbon atom in pentaerythritol, and the

conclusions of Mark and Weissenberg and of Huggins and Hendricks were questioned, first by Nitta (43) and later by a number of other investigators, with the result that it is now definitely established that a mistake was made in the earlier interpretation of the diagrams.

A similar difficulty has appeared in the case of the tetraacetate of pentaerythritol, for which it will be recalled both Ebert, Eisenschitz and v. Hartel and the author (table 2) found rather large electric moments. Gerstäcker, Möller, and Reis (44) reported, as a result of their x-ray investigations, that in this molecule the four carbon atoms attached to the central carbon atom were to be found in a single plane. These conclusions have been questioned by Knaggs (45) who has shown beyond reasonable doubt that the interpretation of the previous experiments was incorrect, and that here again the central carbon atom has its four valences directed to the corners of a regular tetrahedron. The large electric moment of this molecule is explained by Ebert as being caused by a change in the form of the molecule as it is dissolved. The author feels, however, that the results of the x-ray and electric moment studies are in substantial agreement, each indicating that the central carbon atom is of the tetrahedral form, the molecule having a finite electric moment in solution because of the stereochemistry of the groups attached to this tetrahedral central carbon atom and because of interactions between them.

Tetranitromethane has been studied in both solid and dissolved states. As a result of their x-ray studies Mark and Noethling (46) conclude that the four NO_2 groups attached to the central carbon are not alike but are arranged as follows:



These authors point out that their result is in agreement with that obtained by earlier investigators who have studied the relation between various physical properties and the constitution of the molecule in the liquid state. The conclusion is perfectly definite, however, that the electric moment of the molecule is zero—in short, the two results appear to be directly in conflict.

The simplest case from the standpoint of the electric moment data is that of benzene. These data clearly indicate a structure in which all of the six carbon atoms lie in a single plane. From the results of x-ray studies, however, it appears at present impossible to decide in favor of either a plane or space arrangement of the carbon atoms. This point has been briefly discussed by Clark (47).

The comparison of the results of the two types of study is possible in certain other cases, all of which appear to be more difficult of interpretation and which will not be discussed here. Certain progress is being made by Mr. Greene, working in the author's laboratory, and will be reported in another place.

b. Adsorbed film data

The potential differences at interfaces in their relation to the polarity and orientation of molecules have been studied by several investigators (48) (49) (50). It is unfortunate that it is as yet impossible to compare accurate electric moment and potential difference at interface data for some simple molecule. Considerable progress has been made with electric moment data in the case of derivatives of benzene, but for this same type of compound interfacial potential difference data are meagre. On the other hand, interfacial potential difference data for compounds of the aliphatic type are numerous and lead to rather simple interpretations, but electric moment data are available in but comparatively few cases.

Rideal (50) calculates the electric moment of a molecule from interfacial potential difference data in the following manner. The potential difference at the interface must be due to the orientation of molecules which have a definite electric moment. This potential difference is, therefore, proportional to the electric

moment of the molecule in question. It is further proportional to the number of molecules at the interface, that is, the surface concentration which may be calculated from the Gibbs adsorption isotherm. Therefore:

$$E = 4 \pi N \Gamma \mu$$

where E = potential difference at the interface.

N = Avogadro number = 6.06×10^{23}

Γ = surface concentration in gram molecules per square centimeter.

μ = electric moment of the molecule adsorbed at the interface.

For *n*-butyric acid Rideal calculates

$$\frac{1.16 \times 10^{-3}}{3.79 \times 10^{18}} \quad 0.3 \times 10^{-18}$$

In this calculation the assumption is made that the dielectric constant of the surface layer is unity.

The electric moment of *n*-butyric acid has not as yet been accurately determined from dielectric constant and density data, but it appears certain, from preliminary measurements of the author, that it will be of the order of magnitude, $\mu = 1 \times 10^{-18}$ e.s.u. It appears from these and other data which have not been introduced, that the electric moment determined by means of suitable dielectric constant studies will always be larger by a factor of from three to six than those obtained by the method outlined by Rideal. Further, the writer insists that the dielectric constant methods are the only methods now available by which quantitative electric moment data may be obtained. The chief difficulty in the method of Rideal appears to lie in the assumption of unit dielectric constant for the oriented molecule at the interface.

In order to explain why the electric moment of a molecule cannot at present be calculated from potential difference data, Frumkin and the writer (51) have suggested four possible reasons.

1. Incomplete orientation of the molecules at the interface.
2. A disturbing influence of the neighboring water molecules or ions.

3. To determine the values of the electric moment one must know the single potential difference, but the experiments give only a differential effect related to some arbitrary zero point.

4. The polarization of the oriented molecules by the neighboring molecules, assuming the orientation to be always complete.

The fourth possibility appears to be the most promising one. If the oriented molecules are polarized by the presence of the neighboring molecules, that is, a polarization exactly analogous to the polarization due to the deformation of a molecule in the Debye theory, a dielectric constant of the order of magnitude of three or four, instead of one, might be accounted for. Suitable experiments have been designed to test this possibility and are being carried out in this laboratory.

Although this difference in the order of magnitude of the electric moment calculated from the two types of measurement is as yet incompletely accounted for, there are a number of marked parallelisms between the results of the different experimental studies:

1. The results in each case indicate that polar molecules may be considered to be made up of polar parts and non-polar parts—a conclusion of considerable importance for the study of molecular structure.

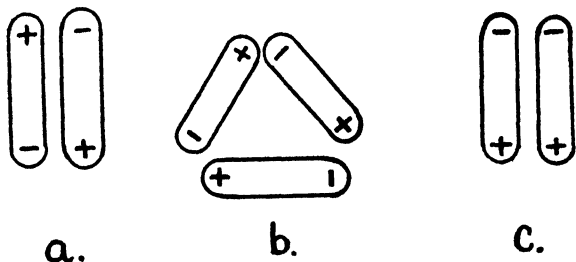
2. A definite electrical character, positive or negative, may be assigned to various atoms and groups of atoms which have been substituted into hydrocarbon residues by each method, and in all cases in which a simple interpretation is possible there is good agreement between the results of the two methods.

3. The order of magnitude of the electrical effects for the alcohols, ketones, acids and halogen derivatives appears to be relatively the same as the dipole effect for the same types of compounds. The somewhat greater relative electrical effects in the case of ethers and esters may be accounted for by the assumption of a more complete bending of the group, thus increasing the degree of orientation.

c. Association

One of the most difficult problems in chemistry is to define exactly what is meant by the term association when applied to

a liquid. There have been numerous methods proposed by which it is supposed to be possible to calculate the degree of association. It has, however, always been a serious difficulty that the results obtained by the different methods have not always agreed. Discussion of the problem has been revived in recent years due to the rapid accumulation of electric moment data for the more common organic liquids, without doubt because Debye (52) has proposed a physical theory for association which depends on the mutual interaction of the dipoles of the liquid. In the neighborhood of these polar molecules there exist strong fields of force which tend to associate the molecules of the liquid. The effects of this association become evident in a study of the dielectric constant and density data for the binary mixtures from which the electric moments of the various solute molecules are calculated. It will be recalled that in the calculation the molar polarization of the solute molecule is determined by extrapolating the P_2 versus mole fraction of solute curve to the position which corresponds to infinite dilution, that is, to a concentration which corresponds to a single solute molecule dissolved in the inert solvent to avoid any effect due to association of solute molecules. The course of the P_2 versus mole fraction of solute curves indicates clearly the effect of several postulated types of association. Thus, if two molecules associate in the manner (a), or if three



molecules associate in the manner (b), the molar polarization of the solute will decrease with increasing solute concentration. On the other hand, if two molecules associate in the manner (c), the molar polarization of the solute will increase with increasing solute concentration. Thus, an association of type (a) is sup-

posed to account for the behavior of nitrobenzene dissolved in benzene, while a combination of associations of types (b) and (c) is supposed to account for the behavior of ethyl alcohol dissolved in benzene. These cases have been discussed by Debye and will not be detailed here. It must, however, be repeated here that such considerations as these can be but qualitative in nature.

To illustrate the type of article now becoming popular the work of Rolinski (53) may be mentioned. This author outlines a method of calculating the degree of association, making use of a modification of the Debye-Clausius-Mosotti law which has been used to determine the electric moments reported in his article. The assumption is made that in the liquid studied, the resultant dipole moment of two associating molecules is exactly zero. The relation used by Rolinski is

$$P = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d} = \frac{4\pi}{3} N \gamma' + \frac{4\pi}{3} N_0 \frac{\mu^2}{3kT} \quad (5)$$

where $\gamma' = \text{constant}$, the polarization due to deformation

$N = \text{total number of molecules}$

$N_0 = \text{number of non-associated molecules}$

and the other symbols have their usual significance.

Using the electric moment found in the ordinary way, the degree of association, α , is given by the equation

$$\alpha = 1 - \frac{N_0}{N} \quad (6)$$

The difficulties with such a treatment have been discussed in some detail in another place (54). They may be summed up by saying that the mutual potential energy of two dipoles depends not only upon their magnitude, as is assumed by Rolinski, but also upon their arrangement and distance between them. Association must, therefore, be dependent also upon the shapes of the molecules, since it will determine the minimum distance to which the polar parts of a molecule may approach.

In conclusion, it may be said that while these considerations may give a qualitative measure of the degree of association and can distinguish various types of association, it has not as yet

given a quantitative explanation. There appears to be absolutely no relation between the conclusions concerning association which have been drawn from cryoscopic measurements and those which result from a consideration of the polarization data for the same systems. The data for phenol may be mentioned. Freezing point measurements show a rapidly increasing molecular weight when this substance is dissolved in benzene, yet the molar polarization values calculated from dielectric constant and density data are perfectly constant over the same range of concentrations.

d. Compound formation

Considerable space has been devoted to a detailed discussion of electric moment data, and it has been shown that these data are intimately related to the results of other types of study. To suggest that the utility of this type of measurement is not limited to the several fields which have just been considered, the application to a field which is as yet practically untouched will be mentioned. Again, it is but one of several important problems about which dielectric constant studies should give important information.

In the previous section there was indicated the manner in which the association of like molecules became apparent from molar polarization data. It may be reasoned that if two substances which will combine to form a compound are dissolved together in a non-polar solvent, the molar polarization of the new compound will differ by a considerable amount from the average molar polarization of the two components, each measured separately. As far as the author is aware, such a study has been attempted in but a single case. Ebert (55) has shown that when ethyl alcohol and hydrochloric acid are mixed, the molar polarization obtained is considerably higher than that of either of the components, the interpretation being that a compound is formed between them. In order to explain the mechanism of many reactions in both inorganic and organic chemistry the existence of an intermediate compound is postulated; it would seem, therefore, that such a study as suggested would be invaluable in

the detection of compound formation in solution. Definite progress has already been made on this problem in our laboratory.

In conclusion, it is my privilege to be able to acknowledge my indebtedness to Professor P. Debye for many valuable suggestions. A considerable portion of the experimental work reported herein was done in his laboratory. It is also a pleasure to acknowledge the contributions of a number of my students, both past and present.

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